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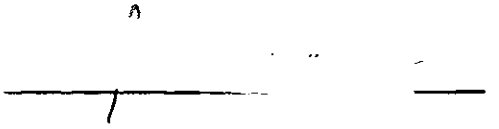

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THE KINETICS AND MECHANISMS OF METHYLMAGNESIUM BROMIDE AND DIMETHYLMAGNESIUM ADDITION TO BENZONITRILE

A THESIS

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BROMIDE AND DIMETHYLMAGNESIUM ADDITION TO BENZONITRILE

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SUMMARY

PART I

THE MECHANISM OF METHYLMAGNESIUM BROMIDE ADDITION TO BENZONITRILE

The kinetics of the reaction of methylmagnesium bromide with benzonitrile in diethyl ether at 25° was examined in detail. The reaction was found to produce on hydrolysis, the alkylation product acetophenone in quantitative yield when the Grignard reagent was prepared from single crystal magnesium. The kinetic data of the reaction show a second-order reaction, first-order in Grignard reagent and first-order in nitrile. The results of rate studies in the presence of added $MgBr_2$ show that the reaction of the Grignard reagent with benzonitrile occurs through both the $(CH_3)_2Mg$ and CH_3MgBr species. All of the accumulated information is consistent with a mechanism which follows two reaction paths. One path involves reaction of benzonitrile with CH_3MgBr species to form $C_6H_5C(CH_3)NMgBr$ whereas the other path involves reaction of benzonitrile with $(CH_3)_2Mg$ to form $C_6H_5C(CH_3)NMgCH_3$ which subsequently and rapidly redistributes with $MgBr_2$ to form the final product $C_6H_5C(CH_3)NMgBr$ and methylmagnesium bromide. Evidence for the formation of a complex between nitrile and Grignard species was found when the concentrations of both reactants were greater than 8×10^{-3} M. The detailed mechanism of this reaction is given in equation 25 in the main body of this dissertation.

PART II

THE MECHANISM OF DIMETHYLMAGNESIUM ADDITION TO BENZONITRILE

The reaction of dimethylmagnesium with benzonitrile in diethyl ether at 25° was examined in detail. The kinetics and mechanism for this reaction have been studied under pseudo-first-order conditions using either excess dimethylmagnesium or excess nitrile. The reaction was found to be first order in nitrile and first order in dimethylmagnesium. The ultraviolet spectra of reacting mixtures showed that complexation between reactants does occur. The physical properties of the reaction product have also been studied. An association study showed that the product is predominantly monomeric at low concentration and exclusively dimeric at high concentration.

PART I

THE MECHANISM OF METHYLMAGNESIUM BROMIDE ADDITION TO BENZONITRILE

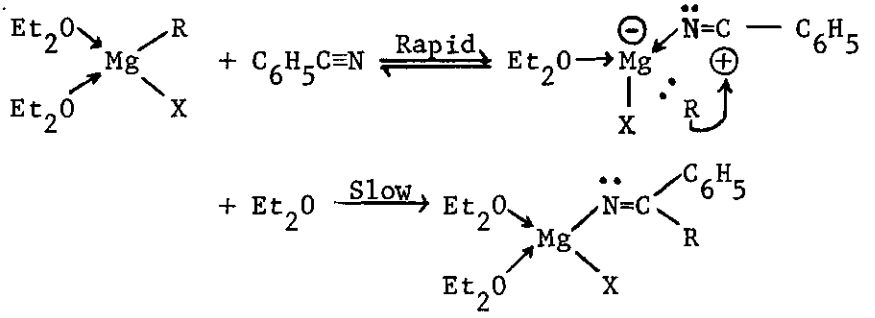
CHAPTER I

INTRODUCTION

Background

The mechanism of Grignard reagent addition to nitriles has been the subject of considerable study for three decades. In spite of efforts on the part of several groups, there appears to be no general agreement concerning the exact mechanism of this reaction. The history of the controversy surrounding this area has been intertwined with the controversy concerning the composition of Grignard reagents in ether solvents,[1] since it is necessary to know the nature of the reactive species in solution before an exact mechanism can be described.

Several mechanisms have been proposed to describe Grignard compound addition to nitriles. The first kinetic study was reported by Swain, who investigated the reaction of n-butylmagnesium bromide with benzonitrile.[2] Swain found the reaction to be second-order overall and suggested that the mechanism which best fit the data involved rapid complexation of monomeric n-C_4H_9MgBr with benzonitrile followed by a slower rearrangement to form the intermediate product (Eq. 1).



(1)

Although the mechanism suggested by Swain is compatible with the reported data, there are a number of weaknesses to the study which continue to leave the mechanism in doubt. The following criticisms appear valid: (1) only four kinetic runs were reported and the concentrations of each reactant and their relative ratios were not widely varied; (2) the kinetic solutions were not homogeneous; (3) the concentration of the Grignard reagent was such that a large percentage of the species present in solution would be associated,[1] although the species present were assumed to be monomeric; and (4) the reactions were followed by analyzing for unreacted Grignard reagent and no attempt was made to verify the nature of the product formed. Although Swain was the first worker to propose the formation of an intermediate complex prior to the alkylation step, no direct evidence was given to support its existence. Also, it was not possible for Swain to designate from his data the nature of the reactive species ($RMgX$, R_2Mg, $R_2Mg \cdot MgX_2$) or the exact nature of alkyl transfer.

Later, Vekemans and Bruylants[3] in 1958 repeated Swain's work by following the reaction spectrophotometrically. Bruylants claimed his method of analysis to be more precise than the gasometric method used by Swain and obtained a rate constant 3.5×10^{-4} 1 mole^{-1} sec^{-1} for the reaction of benzonitrile with n-butylmagnesium bromide at 25°. The spectrophotometric method of analysis was also applied to a kinetic study of the reaction of pivalonitrile with a ten-fold excess of ethylmagnesium bromide. The reaction was described as homogeneous and second-order with a rate constant of 3.1×10^{-5} 1 mole^{-1} sec^{-1} at 25°. Bruylants essentially supported the mechanism proposed by Swain.

The next major development in this area was a direct result of

a report in 1957 describing the composition of Grignard reagents in terms of the unsymmetrical dimeric species ($R_2Mg \cdot MgX_2$).[4] Sometime later, Storfer and Becker[5] adopted the unsymmetrical dimeric structure ($R_2Mg \cdot MgX_2$) for the Grignard reagent to describe Grignard compound addition to nitriles and rejected the Swain mechanism which had proposed monomeric RMgX as the reactive species. Storfer and Becker investigated the kinetics of the reaction of both ethylmagnesium bromide and diethylmagnesium with benzonitrile in tetrahydrofuran. Only 50% of the ethyl groups in diethylmagnesium or in ethylmagnesium bromide were reported to react with benzonitrile. During the reaction two distinct reaction rates were observed, an initial fast rate for the first 30% of the reaction followed by a considerably slower rate for the remainder of the reaction. No simple rate equation could be derived to fit the entire reaction, however, the first part of the reaction was said to fit a second-order rate expression. The results were best interpreted by postulating that diethylmagnesium reacts as $[(C_2H_5)_2Mg]_2$, and that ethylmagnesium bromide reacts as $(C_2H_5)_2Mg \cdot MgBr_2$ and $[(C_2H_5)_2Mg]_2$. The following mechanism was proposed for the reaction of diethylmagnesium with benzonitrile.

$$\underset{\text{(I)}}{2\ R_2Mg} \rightleftharpoons \underset{\text{(II)}}{(R_2Mg)_2} \qquad (2)$$

$$\text{II} + \underset{\text{(III)}}{C_6H_5CN} \overset{\text{fast}}{\rightleftharpoons} \text{Complex} \longrightarrow \underset{\text{(IV)}}{\begin{matrix} C_6H_5 \\ \diagdown \\ R \end{matrix}\!\!>\!C=N\text{-}Mg\text{-}R \cdot MgR_2} \qquad (3)$$

$$\text{IV} + \text{III} \rightleftharpoons \text{Complex} \longrightarrow 2\ \begin{matrix} C_6H_5 \\ \diagdown \\ \quad C=N\text{-}Mg\text{-}R \\ \diagup \\ R \end{matrix} \qquad (2)$$

(V) (or a dimer)

More recently, however, it has been shown that ethylmagnesium bromide is monomeric in tetrahydrofuran over a wide concentration range and is best described by the Schlenk equilibrium which contains essentially an equal amount of RMgX and R_2Mg species ($K = \sim 4$).[6] Thus, Becker's proposal that the reactions of benzonitrile with ethylmagnesium bromide and diethylmagnesium proceed by reaction of $[(C_2H_5)_2Mg]_2$ or $(C_2H_5)_2Mg{\cdot}MgBr_2$ is not probable.

In 1965-66 two reports appeared concerning the mechanism of Grignard compound addition to nitriles. The first report[7] described the reaction of ethylmagnesium bromide with benzonitrile in THF and other solvents as proceeding through the mechanism originally proposed by Swain (Eq. 1). The second report[8] described the reaction of phenylmagnesium bromide with benzonitrile in THF (Eq. 5) as proceeding through a transition state involving attack of $(C_6H_5)_2Mg{\cdot}MgBr_2$ in the rate determining step.

$$(C_6H_5)_2Mg{\cdot}MgBr_2 \xrightarrow{C_6H_5CN} \left[\ \begin{matrix} \sigma+ \\ \sigma- \end{matrix} \begin{matrix} C_6H_5 \\ C \end{matrix} \quad C_6H_5\text{-}Mg\text{-}N \quad Br\text{-}Mg\text{-}Br \ \right] \longrightarrow (C_6H_5)_2C{=}NMgC_6H_5{\cdot}MgBr_2 \qquad (5)$$

Because the mechanism of this reaction is so fundamental and because there seems still many unanswered questions about the exact descriptions of these reactions, we set out to make a detailed kinetic study of the reaction of a Grignard compound with a nitrile in order to resolve the essential features of the mechanism. The main points of the problem basically involve the kinetic order of the reaction in both nitrile and organomagnesium reagent, the nature of the reactive species in those cases where several species exist in equilibrium and the exact nature of the alkyl transfer whether it be via complex formation or as a result of direct bimolecular collision.

In an attempt to determine the mechanism of this reaction it is important to consider the composition of the Grignard reagent under the conditions in which the reaction is being studied. We found earlier that Grignard compounds are monomeric in THF even at high concentrations whereas in diethyl ether bromo and iodo Grignard compounds are monomeric only below 0.1 M. Thus, by operating at Grignard concentrations in diethyl ether below 0.1 M[9] under pseudo-first-order conditions in excess Grignard reagent and in excess nitrile it should be possible to determine directly reaction order of each reactant, avoiding the complication of the presence of associated Grignard species. Furthermore, the rate of reaction of only the R_2Mg species with nitrile can be determined by independent kinetic experiments and the determination of the rate of reaction of only the RMgX species with nitrile should be possible by reaction of nitrile with Grignard reagent to which has been added a sufficient excess of $MgBr_2$ such that the Schlenk equilibrium is completed shifted in favor of the RMgX species. Such rate

information should make it possible to determine the role of both R_2Mg and RMgX species in the reaction with nitriles. Some information as to the nature of alkyl transfer, whether it be through a complex or simple bimolecular attack, should be possible by direct spectroscopic observation of an absorption band due to the complex.

Finally, we know from our previous work involving the reaction of Grignard reagents with ketones that the purity of the magnesium metal used to prepare the Grignard reagent is crucial. Grignard reagent prepared from triply sublimed magnesium produced by-products in the reaction of benzophenone with excess methylmagnesium bromide whereas the same Grignard reagent prepared from single crystal magnesium eliminated this problem.

An ideal system was chosen for this study; i.e., the reaction of benzonitrile with methylmagnesium bromide (prepared from single crystal magnesium) in diethyl ether at 25°. In this reaction no reduction or enolization is possible and by the use of Grignard reagent prepared from single crystal magnesium, by-product formation observed with Grignard reagent prepared from triply sublimed magnesium was completely eliminated. Initial studies also showed that only addition product is formed and in essentially quantitative yield.

Purpose

The kinetics of the reaction of benzonitrile with Grignard reagent in diethyl ether solution was studied in an attempt to establish the detailed mechanism of this reaction.

CHAPTER II

EXPERIMENTAL

Chemicals

Single crystal magnesium (Ventron Electronics Corporation; Bradford, Pennsylvania) was milled with a carbide tool. The turnings were washed several times with anhydrous diethyl ether, then dried and stored under nitrogen. The purity of single crystal magnesium is 99.9995%, with less than 2 ppm of Ni, Co and Fe as impurities.[10]

Eastman spectro grade benzonitrile was dried and purified by distillation over solid, ether-free, methylmagnesium bromide. The nitrile was distilled at 30° and 0.5 mm. The middle fraction of the distillation was collected for the kinetic studies. Since glpc analysis (flame ionization detector) of the distilled material showed no extraneous peaks, the nitrile is believed to be at least 99.99% pure. The distilled material was stored in a reaction flask equipped with a three-way teflon stopcock, shielded from light and stored in an inert atmosphere box.

Methyl bromide (Matheson, 99.5% purity) was dried and purified by passing through a 30 cm tube of NaOH pellets and then through a 70 cm tube of Linde 4A molecular sieve. N-tetradecane (Chemical Samples, 99.9% purity) were dried and distilled at 55° and 0.02 mm pressure from Linde 4A molecular sieves. It was used as an internal standard in the kinetic study. Acetophenone (Eastman) was purified by distillation

under vacuum using a spinning band column. Mercury bromide (Baker Analyzed reagent) was used without further purification. Diethyl ether (Fisher Anhydrous) was distilled under nitrogen from $LiAlH_4$ through a 60 cm glass helix packed column.

Magnesium bromide was prepared by a method described earlier involving the reaction of mercury bromide with magnesium in diethyl ether.[11] Elemental analysis of the product showed the ratio of Mg:Br to be 1:00:1.94.

Instrumentation and Apparatus

An inert atmosphere box equipped with a recirculating system[12] to remove moisture and oxygen was used during the manipulation of air-sensitive reagents. As an added precaution, a special line for prepurified nitrogen was added to the glove box and all materials were transferred in Schlenk tubes under a blanket of prepurified nitrogen.[13]

A F+M model 700 flame ionization gas chromatograph was used to analyze the products.

All infrared spectra were obtained using a Perkin Elmer 621 high resolution grating spectrophotometer and sodium chloride absorption cell.

All visible and ultraviolet spectra were recorded on a Cary Model 14 recording spectrophotometer. A Zeiss PMQ II single beam spectrophotometer was employed for making absorbance measurements in order to determine extinction coefficients and obtain Beer's law plots at a single wavelength.

Either matched quartz cells (Beckman, 10.0 mm) sealed with a 1 mm

bore two-way Kimax micro Teflon stopcock or Zeiss 1.00 mm cells were used for the ultraviolet measurements.

A Sargent constant temperature water bath was used for controlling the temperature ($\pm$ 0.02°) of the kinetic solutions; temperatures were monitored with a calibrated thermometer reading to 0.1° with estimates to 0.02°.

The kinetic flasks were fabricated by sealing a three-way teflon stopcock to the top of a 100 ml heavy walled glass bulb.

The syringes equipped with stainless steel needles employed for transfer of the samples were calibrated prior to use. Deliveries could be reproduced to better than $\pm$ 0.5%.

Analyses

All of the solutions were analyzed for magnesium by titration with EDTA. Solutions of the Grignard compounds and magnesium halides were analyzed for halogen by the Volhard method. The concentration of basic-magnesium bonded to carbon was determined by Gilman titration.

Preparation of Methylmagnesium Bromide

Since the Grignard reagent is used in such low concentration, a precise method of preparing the reagent is crucial. The ether still was connected to a dry ice-acetone condenser and a 250 ml round bottom one-neck flask containing single crystal magnesium (3.0 g, 0.125 g-atom) and a stirring bar was attached below the condenser. After appropriate heating followed by N_2 flushing, approximately 100 ml of diethyl ether was distilled into the reaction flask. The ether was then removed

under vacuum. This procedure rinsed the internal part of the still and condenser that could not be dried by external heating. Then the entire apparatus was dried under vacuum (0.01 mm) by flash flaming the apparatus followed by N_2 flushing. The above procedure was repeated twice. The condenser was charged with dry ice and after distillation of approximately 50 ml ether into the reaction flask, methyl bromide (appropriately purified) was introduced through a side arm near the base of the condenser. After the reaction had begun, as evidenced by bubbling and heat release, stirring was begun. Diethyl ether was distilled into the reaction flask and methyl bromide added at a rate required to maintain gentle reflux without external heating. Addition of methyl bromide was continued until all of the magnesium was consumed. The distillation of the ether was continued until the flask contained approximately 200 ml of solution. Stirring was continued until the reaction had ceased and the flask had cooled to room temperature. Since an excess of methyl bromide was used in the preparation, complete solvent removal was effected under vacuum followed by redistillation of ether into the flask. The diethyl ether solution of methylmagnesium bromide prepared by this procedure was clear and colorless. The composition of the Grignard was determined by Gilman titration for C-Mg, EDTA for total magnesium and Volhard for halogen. The results gave C-Mg:Mg:Br ratio of 0.998:1.000:0.998. Clearly there is no significant amount of coupling product. The Grignard reagent was transferred via syringe into a reaction flask equipped with a three-way teflon stopcock, and stored in the dry box.

Fractional Crystallization of the Reaction Product

Methylmagnesium bromide (50 ml of 1.623 M solution in diethyl ether) was diluted to 200 ml by adding freshly distilled diethyl ether in a 500 ml one-neck round-bottom flask containing a stirring bar and equipped with a three-way teflon stopcock. One hundred ml of an ether solution of benzonitrile (4.0998 g, 3.977×10^{-2} mole) was added to the Grignard solution via syringe under prepurified nitrogen flow. The reaction mixture was allowed to stir for six days during which time a large amount of precipitate was formed. GLC analysis indicated that the reaction was complete. The resulting mixture was fractionally crystallized into three fractions and the fractions were dried under vacuum for 24 hours. The results of elemental analysis of the fractions are shown in Table 1.

Table 1. Fractional Crystallization of the Reaction Product from Methylmagnesium Bromide and Benzonitrile in Ether

Fractions	Sample Wt. (g)	Mg (%)	Br (%)	Mg:Br Ratio
1	1.6297	7.31	24.71	1.00:1.01
2	0.3374	10.14	31.44	1.00:0.95
3	0.0637	8.35	27.60	1.00:1.01
Calcd. for $C_6H_5C(CH_3)NMgBr \cdot Et_2O$		8.22	27.01	1.00:1.00
Calcd. for $C_6H_5C(CH_3)NMgBr$		10.96	36.02	1.00:1.00

Redistribution of $C_6H_5C(CH_3)NMgCH_3$ with $MgBr_2$

A solution (50 ml, 0.318 M in diethyl ether) of $C_6H_5C(CH_3)NMgCH_3$ was prepared by the reaction of $(CH_3)_2Mg$ and C_6H_5CN in 1:1 ratio. $MgBr_2$ (3.0521 g, 0.0166 mole) was dissolved in 150 ml of freshly distilled diethyl ether and added to the solution of $C_6H_5C(CH_3)NMgCH_3$. A light yellow precipitate formed immediately after mixing. The solid was filtered through a fine porosity fritted glass funnel under vacuum in the dry box, dried under vacuum and analyzed (Table 2). The infrared and nmr spectra of the filtrate were consistent with that observed earlier for methylmagnesium bromide. Ether was then removed from the filtrate under vacuum and the resulting solid analyzed (Table 2).

Table 2. Reaction of $C_6H_5C(CH_3)NMgCH_3$ and $MgBr_2$ in Diethyl Ether

	Sample Wt.(g)	Mg(%)	Br(%)	Mg:Br Ratio
Precipitate	3.7449	9.79	34.88	1.00:1.09
Calcd. for $C_6H_5C(CH_3)NMgBr$		10.96	36.02	1.00:1.00
Filtrate	0.7270	13.10	38.78	1.00:0.90
Calcd. for $CH_3MgBr \cdot Et_2O$		12.88	41.37	1.00:1.00

Procedures for Kinetic Studies

The kinetic flasks, syringes and needles were rinsed with ether, heated in an oven at 150°, for at least two hours and then placed into the entry port of an inert atmosphere box which was subsequently evacuated to a pressure of 0.25 mm of Hg. After filling the chamber with

prepurified nitrogen, the equipment was transferred into the dry box and assembled after a thorough purge via a needle with a stream of prepurified nitrogen and passed through a 90 cm tube of Linde 4A molecular sieve. All of the solutions were sampled via syringe through a three-way teflon stopcock under a flow of prepurified nitrogen in the dry box. Since the solubility of the reaction product was found to be about 3×10^{-2}M, all kinetic studies were carried out at concentrations below this value.

For the kinetic studies in excess Grignard reagent, concentrated organomagnesium reagent was added to diethyl ether in order to dilute to the desired concentration. A 70 ml portion of dilute organomagnesium solution was transferred from the dilution flask via syringe to the reaction flask. Neat n-tetradecane was then added to the reaction flask as an internal standard. The reaction flask was wrapped with aluminum foil and placed in a constant temperature water bath ($25 \pm 0.02°$). The flask and its contents were allowed to reach temperature equilibrium before a nitrogen line was attached to the stopcock at the top of the reaction flask. After turning the stopcock in a manner to by-pass the opening to the solution, the line and stopcock were purged with nitrogen. The stopcock was then turned to accept a syringe needle from the top with the nitrogen flow from the side, and the desired amount of benzonitrile standard solution added via a 50 µl syringe. A 2 ml sample was withdrawn immediately and quenched in a vial with a septum cap containing 6 ml of saturated ammonium chloride solution. This sample was used as the zero time reading. Other samples were quenched in the same manner at appropriate intervals of time. Samples were obtained over the range

5-80% reaction. The quenched samples were analyzed by following the disappearance of nitrile by gas chromatography. The time was recorded after the sample was injected into the ammonium chloride solution.

After withdrawing the needed amount of dilute organomagnesium solution for the kinetic studies, three 5 ml samples of dilute organomagnesium solution were withdrawn for concentration determination. Excess of 0.01 N H_2SO_4 was added to the sample followed by ether removal under aspirator pressure on a steam bath. The excess H_2SO_4 was back titrated with 0.01 N NaOH solution to a phenolphthalein end-point. The average value was adopted as the concentration of organomagnesium solution.

Kinetic studies in excess benzonitrile were also carried out. Although concentrated solutions of benzonitrile (0.5M) absorb strongly at wavelengths shorter than 280 mμ, negligible absorbance in the region between 320 mμ and 370 mμ is observed. Diethyl ether solutions of methylmagnesium bromide show no absorbance in the ultraviolet spectrum above 270 mμ. Ultraviolet spectra of mixtures of methylmagnesium bromide with excess benzonitrile were obtained in the following fashion. Quartz 10 mm UV cells, glass sealed with a 1 mm bore two-way Kimax teflon stopcock, were dried for a few seconds by heating and then transferred to the dry box. The syringes with stainless steel needles, 25 ml volumetric flasks sealed with a three-way teflon stopcock and other glassware were transferred to the dry box by the routine procedures. The 25 ml flasks and UV cells were purged with prepurified nitrogen via a needle before loading the samples. The desired amount of standard benzonitrile solution was added to the 25 ml volumetric flask under

nitrogen flow which was subsequently diluted to the mark with diethyl ether. A 4 ml portion of dilute benzonitrile solution was transferred from the volumetric flask to the UV cell via a calibrated syringe. The UV cells were removed from the dry box along with 50 μl syringe containing the Grignard reagent. The UV cells were placed in a constant temperature water bath. After a suitable amount of time was allowed for the cells to come to temperature equilibrium, a known amount of standard Grignard reagent was injected into the cell. The cell was rapidly shaken to insure mixing. The rate of the reaction was followed by measuring the increase in absorbance at 344 mμ, λmax of the product. The cells remained in the constant temperature water-bath at all times except when taking a reading. Generally, 25 to 30 sets of time-absorbance values were taken in each kinetic experiment.

For the kinetic studies using a low ratio of reactants, a 70 ml portion of freshly distilled diethyl ether was transferred to a reaction flask. A calibrated syringe was used to transfer the desired amount of methylmagnesium bromide to the reaction flask. The concentration of organomagnesium solution was computed by the dilution method. The deviation of the organomagnesium concentration between dilution and titration was checked and found to be within 2%. The remainder of the procedures were similar to those described for the kinetic study in excess methylmagnesium bromide, except determination of the initial concentration of benzonitrile was accomplished by quenching the reaction mixture at zero time in 10% H_2SO_4 and measuring the absorbance of benzonitrile at 277.5 mμ. Kinetic data were also obtained by gas chromatographic analysis.

Product Analysis

GLPC analysis was performed using 6-ft one-eighth inch matched stainless steel columns of 10% FFAP on 80-100 mesh Diatoport S. Product yields were determined by comparison of reaction mixtures with the internal standard, n-tetradecane. The reaction product was identified by comparing the retention time with that of an authentic sample under the conditions of flow rate, 40 ml/min; injection and detector temperature, 230°. The retention times for n-tetradecane, benzonitrile and acetophenone are 6, 18 and 23 minutes at a column temperature of 105°. The components of the reaction mixture could be satisfactorily separated under these conditions.

A 100 ml diethyl ether solution of benzonitrile (4.9703 g, 4.822 x 10^{-2} mole) and methylmagnesium bromide (41.8 ml, 1.154 M) were allowed to react with stirring at room temperature for five days. The mixture was hydrolyzed with 5% hydrochloric acid solution. Acetophenone was found in 94.5% conversion with 5.5% unreacted benzonitrile recovered.

Three different ratios of standard mixtures of n-tetradecane, benzonitrile and acetophenone were prepared in diethyl ether and subjected to gas chromatography to give the relationship, (mole nitrile)/(mole n-tetradecane) = 1.95 (area nitrile)/(area n-tetradecane) and (mole nitrile)/(mole ketone) = 1.048 (area nitrile)/(area ketone).

CHAPTER III

RESULTS

General Features of Rate Studies

An important consideration in Grignard reactions is that the kinetic studies must be carried out at concentrations at which the organomagnesium species in solution are monomeric. If not, associated species are present and the analyzed concentration of the Grignard solution does not represent the concentration of monomeric species. This point is crucial if the reaction proceeds through the monomeric species. In general, this consideration has been ignored by workers in the field and as a result kinetics carried out at concentrations in which associated species are present have produced results which have been explained by salt effects[14] and other phenomena. Our association measurements[9b] have indicated the Grignard reagent concentration at which association becomes appreciable and we have carried out our studies below this concentration, thus avoiding the problem discussed above.

The reactions of benzonitrile with methylmagnesium bromide in diethyl ether were studied in two ways: (1) in excess Grignard reagent by quenching the reaction mixture with saturated ammonium chloride solution and then measuring the disappearance of benzonitrile by glpc using n-tetradecane as an internal standard, (2) in excess benzonitrile by following directly the appearance of the product band [$C_6H_5C(CH_3)N$-MgBr] at 344 mμ by uv analysis. Since the absorbance of acetophenone, the product after hydrolysis, appears in the same region in the uv as

benzonitrile (240 mμ to 280 mμ), it is not possible to use spectrophotometric methods to follow the appearance of acetophenone. In the first case, the data were recorded generally between 5 and 80% reaction for each individual run. In the second case, each individual run was allowed to reach completion. Under pseudo-first-order conditions,[15] the kinetic dependence was simplified by eliminating the dependence of one of the reactants at a time. The dependence on benzonitrile was determined by using an excess of organomagnesium reagent and vice versa.

Magnesium Purity

The purity of magnesium used in these studies is also crucial because there is evidence that rates of reactions of Grignard compounds with organic substrates are quite sensitive to trace impurities of transition metals.[16] Thus, several different grades of magnesium were used in an attempt to determine the effect of magnesium metal purity on the kinetics of Grignard compound addition to nitriles. Indeed, it was found that when triply sublimed magnesium (99.95% pure) was used to prepare the Grignard reagent, 2-13% by-product formation was observed when excess Grignard reagent was allowed to react with benzonitrile. Although by-product was formed under conditions of excess Grignard reagent prepared from triply sublimed magnesium, no by-product was formed when the Grignard:nitrile ratio was 1:1. The by-product formed immediately when the reactants were mixed; however, the amount formed was nearly constant throughout the entirety of the reaction. The % by-product changed with the ratio of $[G]_o/[N]_o$ as shown in Table 3. Each individual run followed

Table 3. The Relationship of % By-Product to the Ratio of Methylmagnesium Bromide[a] to C_6H_5CN

$[G]_o$, M	$[N]_o \times 10^4$, M	$\frac{[G]_o}{[N]_o}$	By-Product %
0.101	7.02	145	13.00
0.101	9.33	110	9.69
0.117	41.12	30	2.47

[a]Methylmagnesium bromide prepared from triply sublimed magnesium.

a well-behaved first-order pattern in benzonitrile, however, a plot of k_G vs. $[G]_o$ did not produce a straight line. In addition, faster rates were observed when methylmagnesium bromide prepared from triply sublimed magnesium was allowed to react with benzonitrile as compared to those cases when the Grignard reagent was prepared from single crystal magnesium.

A small amount of Grignard solution was prepared from an ultrapure grade of magnesium[17] used earlier.[16] In the one run performed with this Grignard reagent, using an excess of the Grignard reagent, no by-product was found. Further kinetic studies were carried out using Grignard reagent prepared from zone-refined magnesium.[18] Although no by-product was formed under conditions of excess Grignard reagent and each individual run exhibited well-behaved first-order kinetics, k_G was still found to be dependent on benzonitrile concentration.

The most consistent kinetic results were obtained from Grignard

reagent prepared from single crystal magnesium.[19] No by-product was formed in the reaction and k_G was only very slightly dependent on the initial concentration of benzonitrile in excess Grignard reagent. The data obtained in this study are summarized in Table 4.

Table 4. Observed Rate Constants for the Reaction of a Constant Concentration of Methylmagnesium Bromide (5.82×10^{-2}, M) with a Variable Initial Concentration of Benzonitrile.

Run	$[N]_\circ \times 10^4$, M	$\frac{[G]_\circ}{[N]_\circ}$	$k_G \times 10^4$, min^{-1}
1	5.90	97.9	1.41
2	10.07	57.1	1.39
3	13.78	41.6	1.36
4	17.48	32.6	1.32
			Ave. 1.37 ± 0.037

The Reaction Product and Its Properties

The reaction product of methylmagnesium bromide with C_6H_5CN in diethyl ether has been studied by fractional crystallization. The data show that the product has the empirical formula $C_6H_5C(CH_3)NMgBr$. More information about the physical properties of the reaction mixture could not be obtained due to the low solubility of the product ($< 3 \times 10^{-2}$M). When the ratio of Grignard:nitrile was 2:1 the product precipitated from solution essentially quantitatively leaving one mole equivalent of Grignard reagent in solution.

Kinetics in Excess Grignard Reagent

Reactions using excess Grignard reagent were performed in diethyl ether at 25° at Grignard:nitrile ratios ranging from 20:1 to 70:1. The maximum concentration of methylmangesium bromide employed was 0.1 M since association studies have shown that the former is predominantly monomeric at and below this concentration. The kinetic data were obtained by quenching individual samples of the reaction mixture in saturated ammonium chloride solution at appropriate intervals of time and following the disappearance of nitrile by glpc. Under these conditions, the reaction was found to be first-order in benzonitrile (Figure 1). The significance of the linearity will be discussed later. Pseudo-first-order rate constants were calculated from the first-order equation (Eq. 6) for each of the eight to ten sets of % reaction-time values obtained in a given experiment. In equation 6, $[N]_o$ is the initial concentration of ben-

$$k_G = \frac{1}{t} \ln \frac{[N]_o}{[N]} \qquad (6)$$

zonitrile and [N] is the concentration of benzonitrile at time t. The data obtained in this study are summarized in Table 5.

The values of k_G increase with $[G]_o$ as expected. If the reaction is first-order in Grignard then $k_G/[G]_o$ should be constant for this series of experiments. The values are observed to be constant (Table 5). The rate law for the reaction in excess Grignard is then given by the expression:

$$\text{Rate} = k[C_6H_5CN][\text{Grignard}] \qquad (7)$$

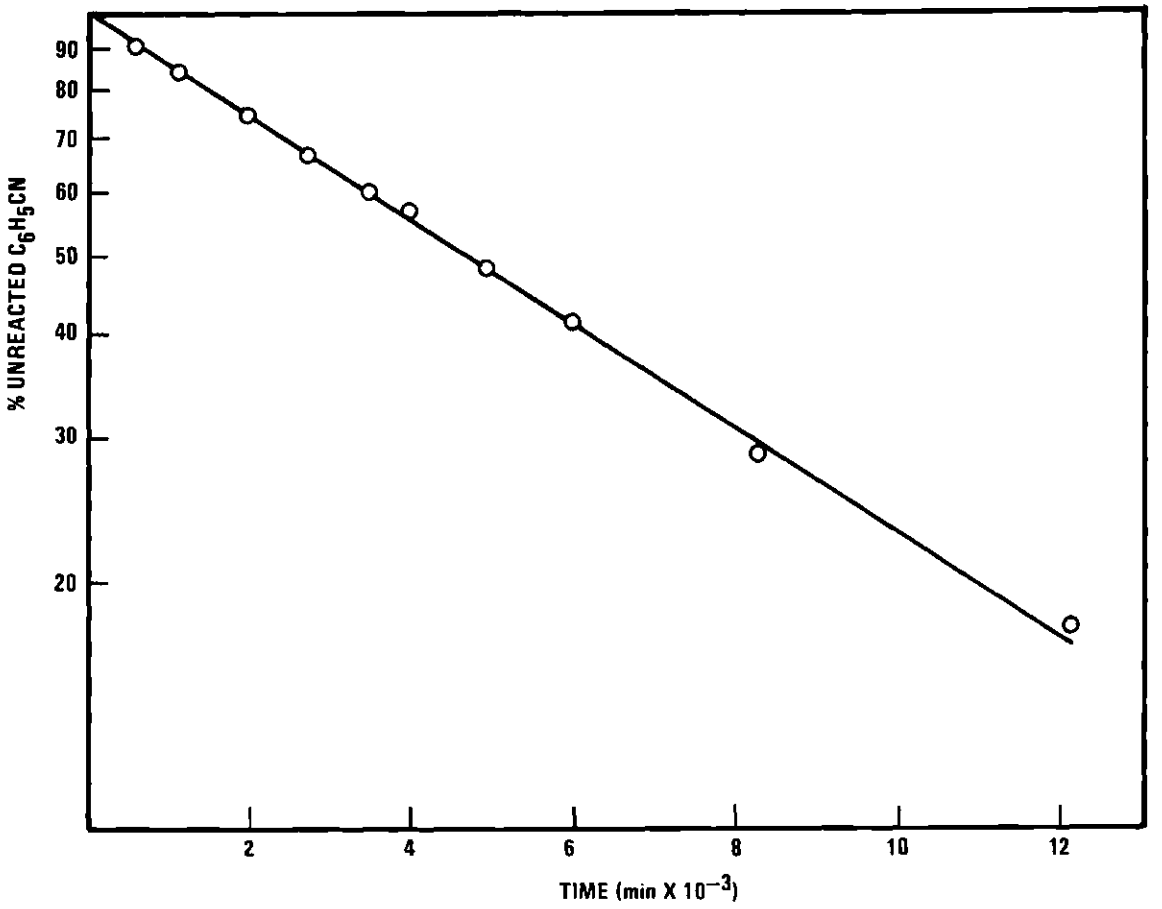


Figure 1. Plot Demonstrating Pseudo-first-order Behavior of Benzonitrile (1.49×10^{-3}M) with Excess Methylmagnesium Bromide (5.67×10^{-2}M) in Diethyl Ether at 25°.

The value of k obtained from these experiments is $(2.41 \pm 0.06) \times 10^{-3}$ 1 $mole^{-1}$ min^{-1} at 25°.

If a significant amount of complex between C_6H_5CN and Grignard were present in these systems the value of $k_G/[G]_o$ should show a decreasing trend with increased $[G]_o$. Since such a trend is not evident it can be concluded that $K[G]_o < 1$, where K is the equilibrium constant for complex formation and further, that $K < 10$.

Table 5. Observed Rate Constants for the Reaction of Benzonitrile with Excess Grignard Reagent at 25°.

Run	$[G]_o \times 10^2$, M	$\frac{[G]_o}{[N]_o}$	$k_G \times 10^4$ min^{-1}	$k_G \times 10^4$ min^{-1} (Calc.)	$\frac{k_G}{[G]_o} \times 10^3$ 1 $mole^{-1}$ min^{-1}
5	2.19[a]	36.6	0.533	0.512	2.43
6	2.98	20.1	0.715	0.686	2.44
7	4.63	31.2	1.13	1.03	2.45
8	5.67	38.2	1.45	1.23	2.55
	5.82[b]		1.37	1.26	2.35
9	6.80	45.8	1.66	1.45	2.43
10	8.44	56.8	1.95	1.73	2.31
11	9.98	67.1	2.30	2.00	2.31
					Ave. 2.41 ± 0.06

[a]In the reaction of C_6H_5CN with excess methylmagnesium bromide, the C_6H_5CN concentration was 1.49×10^{-3} M except in this case when it was 6.00×10^{-4} M. [b]Average of four runs from Table 4.

Kinetics in Excess of Nitrile

A kinetic study of the reaction was also carried out in excess benzonitrile. Under these conditions the kinetic dependence on nitrile is eliminated, thereby allowing the determination of the kinetic order of the Grignard reagent directly.

The rate of the reaction in excess benzonitrile was followed spectrophotometrically by following the increase in the absorption band at 344 mμ characteristic of the product. The absorbance increased rapidly initially, then reached an almost constant value for a period of time, and finally increased rapidly again. Typical behavior is shown in Figure 2. The rapid increase in absorbance in the final stage is attributed to a condensation product with a high molar extinction coefficient.

Further information was obtained by quenching the reaction mixtures in the uv cell with saturated ammonium chloride and following the appearance of acetophenone by gas chromatographic analysis. A number of determinations were carried out when the absorbance readings had leveled out indicating complete reaction with Grignard reagent and before the absorbance of the condensation product appeared. At this point (~ 85% reaction) glpc analysis did not reveal the presence of condensation product.[20]

The initial rise in absorbancy to the leveling off value suggested the behavior associated with a single first-order reaction. In this case the variation of absorbancy with time is given by the expression:

$$Abs = Abs_{\infty} - (\varepsilon_B - \varepsilon_A)[A]_o \; e^{-k_N t} \qquad (8)$$

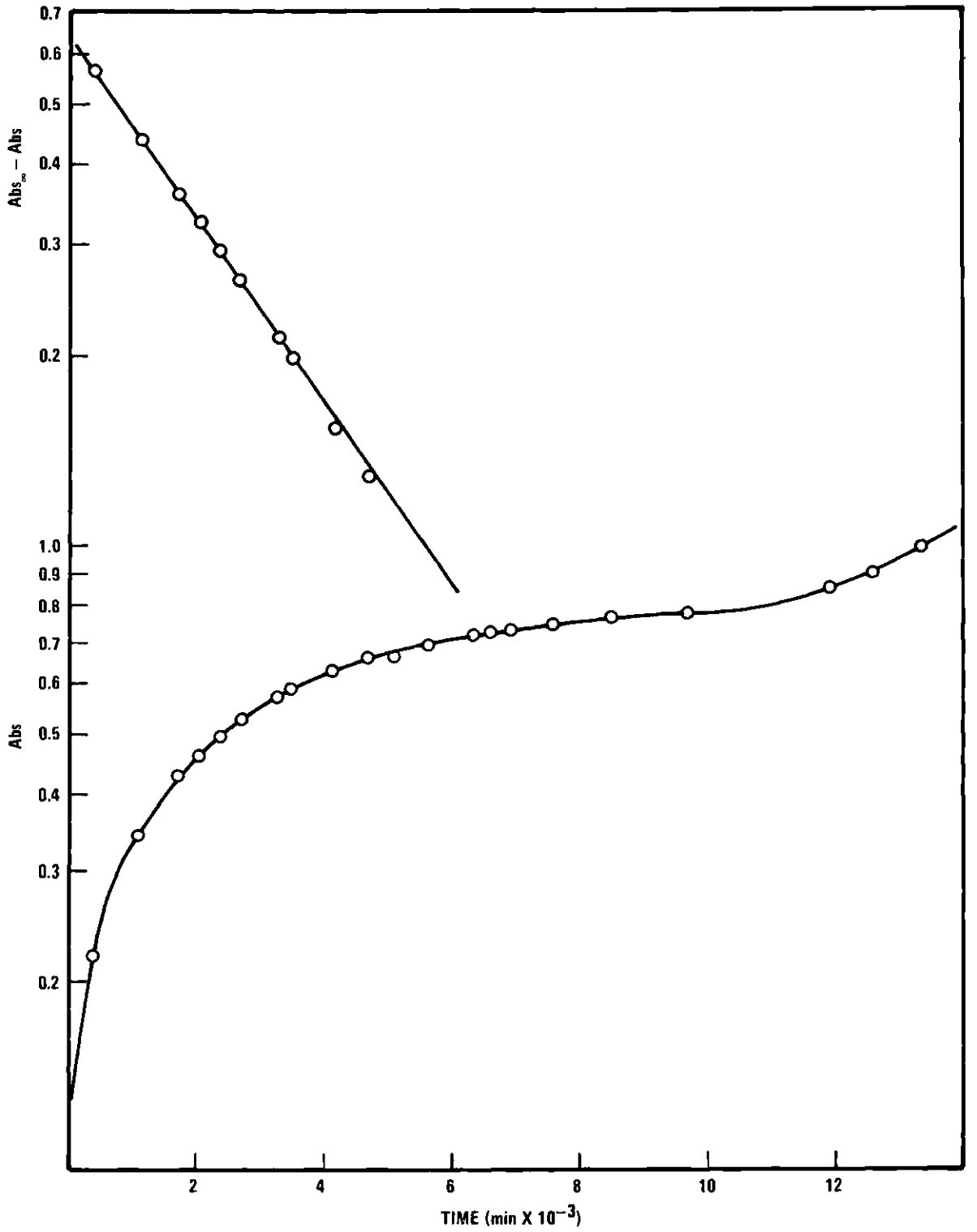


Figure 2. The Reaction of Methylmagnesium Bromide (5.94×10^{-3} M) with Excess Benzonitrile (0.127 M) in Diethyl Ether.

and a plot of log (Abs_∞ - Abs) versus t should produce a straight line with a slope of $k_N/2.303$. Plots of log (Abs_∞ - Abs) versus t showed the expected linearity, and allowed determination of k_N, the pseudo-first-order rate constant.

If the reaction is first-order in benzonitrile, in addition to being first-order in Grignard, the second-order rate constant is $k_N/[N]_o$. The results from several experiments are summarized in Table 6. The reliability of the observed rate constants were tested at constant excess nitrile concentration with variable methylmagnesium bromide concentration and found to be independent of the concentration of methylmagnesium bromide (Runs 16-19).

For nitrile concentrations less than 0.2 M the rate law can be expressed by equation 9 with the value of k equal to 2.52×10^{-3} 1 $mole^{-1}$ min^{-1}. This value is the same, within experimental error, as the value obtained in the experiments with excess Grignard. This excellent agreement leads to the conclusion that the same mechanism is operative both in excess Grignard and in excess nitrile.

$$\text{Rate} = k[C_6H_5CN][\text{Grignard}] \qquad (9)$$

For nitrile concentrations greater than 0.2 M values of $k_N/[N]_o$ become smaller as the nitrile concentration becomes larger. This is the behavior expected if complexation between nitrile and Grignard is appreciable. The trend in the values indicates an equilibrium constant of magnitude about 2-3.

Table 6. Rate Constants for the Reaction of Methylmagnesium Bromide in Excess Benzonitrile at 25°

Run	$[N]_o$	$[G]_o \times 10^3$, M	$k_N \times 10^4$ min^{-1}	$k_N \times 10^4$ min^{-1} (Calc.)	$\frac{k_N}{[N]_o} \times 10^3$ $1\ mole^{-1}\ min^{-1}$
12	0.0637	2.92	1.56	1.34	2.44
13	0.0729	2.87	1.80	1.52	2.47
14	0.0780	2.92	2.12	1.63	2.71
15	0.101	4.33	2.72	2.10	2.69
16	0.128	3.33	2.91	2.46	2.27
17	0.128	4.07	2.83	2.46	2.21
18	0.127	4.67	3.21	2.44	2.53
19	0.127	5.94	3.34	2.44	2.63
20	0.150	2.01	3.62	2.98	2.42
21	0.230	3.93	4.43	4.34	Ave. 2.52 $\pm$ 0.12
22	0.459	3.93	7.83	7.53	
23	0.640	3.93	7.75	8.83	
24	0.822	3.93	9.36	10.40	

Low Ratio of Reactants

Since the same rate law was observed in large excess of nitrile and in large excess of Grignard, it was reasonable to expect that the same rate law should hold when the two reactants are in approximately equal concentrations. Figure 3 and Table 7 show the results of several such experiments. When the Grignard reagent was in five-fold excess, a standard second-order plot was linear for 80% of the reaction; with a three-fold excess of Grignard reagent, the second-order plot was linear 70% of the reaction; with a two-fold excess, the second-order plot was linear for 55%; and in equal molar ratios the second-order plot was linear for 40% reaction. The reactions do not follow the simple second-order behavior for the entirety of the reaction. The standard second-order plots are initially linear, but the second-order rate constants obtained (designated as k_{app}) were about 25% smaller than those obtained under pseudo-first-order conditions. Only in the later stages of the reaction did the rates approach the expected values.

The fact that the rate is initially slower than expected would be consistent with the presence of significant amounts of complex at that time. In the later stages, with decreased amounts of both Grignard and nitrile, the amount of complex could become negligible and the rate thus reach the expected value. Assuming that complexation accounts for the observed effects, an equilibrium constant of magnitude 2-5 is calculated.

The Effect of Magnesium Bromide on Reaction Rate

The addition of magnesium bromide in reaction mixtures involving organomagnesium compounds has been reported to affect the course or rate of a variety of reaction. Addition of magnesium bromide decreases the

Table 7. Rate of Reaction at Low Reactant Ratios

Run	$[N]_o$	$[G]_o$	k_{app}[a] x 10^3 $l\ mole^{-1}\ min^{-1}$	k_{app} x 10^3 (Calc.) $l\ mole^{-1}\ min^{-1}$
25	0.02667	0.1262	1.69	1.59
26	0.02897	0.0885	1.70	1.63
27	0.03092	0.0627	1.65	1.73
28	0.03375	0.0272	1.47	1.79

[a]Calculated from the first several points using the equation:

$$k_{app} = \frac{1}{t\,([G]_o - [N]_o)} \left(\ln \frac{[G]}{[N]} - \ln \frac{[G]_o}{[N]_o}\right) \qquad (10)$$

where $[G]_o$ and $[N]_o$ are the initial concentrations of Grignard reagent and benzonitrile respectively, and $[G]$ and $[N]$ represent the concentrations of Grignard reagent and benzonitrile at time t.

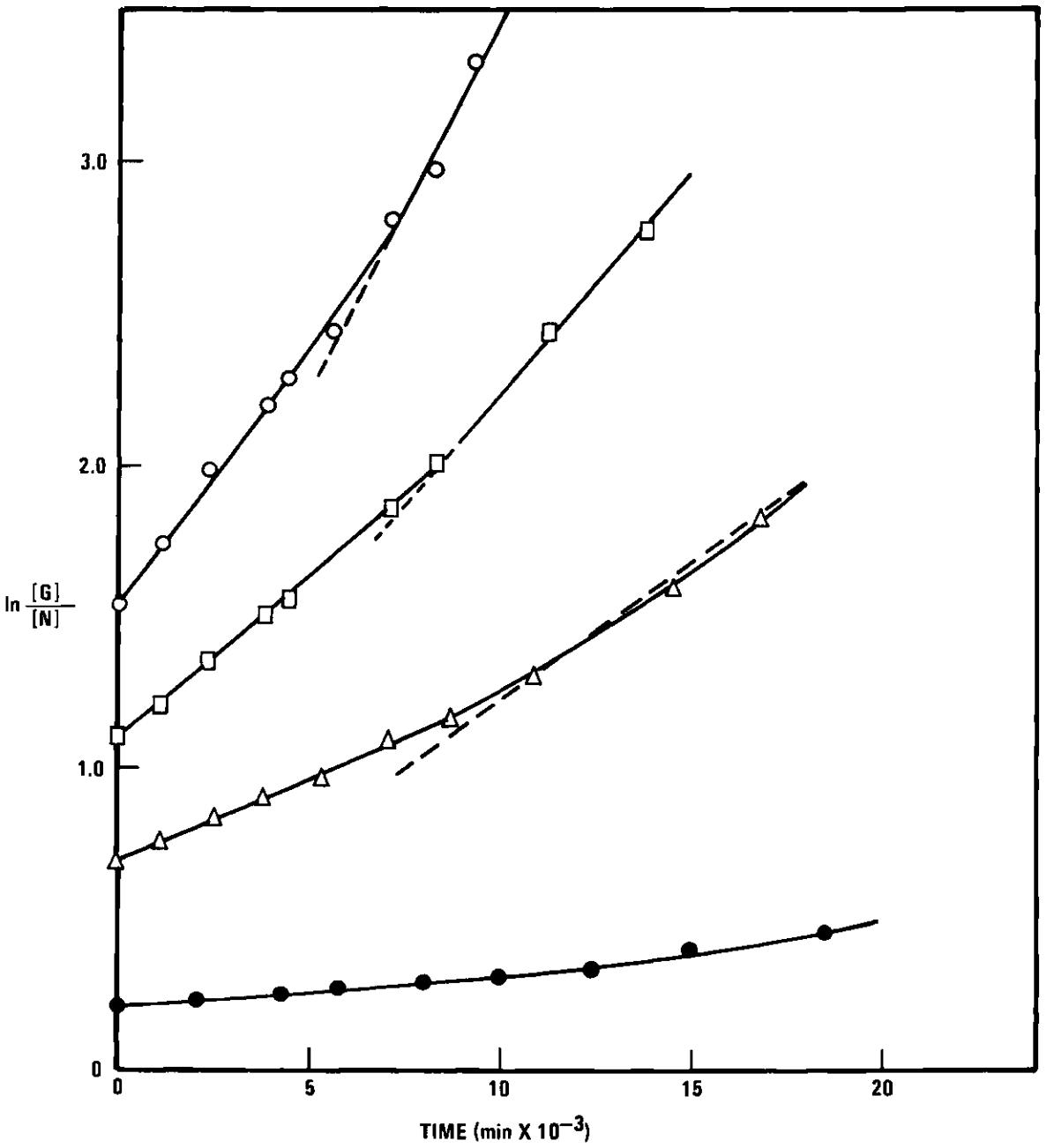


Figure 3. Second-order plot of the reaction of methylmagnesium bromide with benzonitrile at low ratio in diethyl ether. ○, five-fold excess of G; □, three-fold excess of G; △, two-fold excess of G; ●, equivalent amount. Dotted lines correspond to slope expected for k= 2.45 x 10^{-3} 1 $mole^{-1}$ min^{-1}.

rate of reaction of diphenylmagnesium with benzonitrile in THF.[8] A similar decrease has been reported numerous times in the reactions of Grignard reagents with ketones or esters.[21-27]

Although it may have other effects on the reaction system, the addition of magnesium bromide to methylmagnesium bromide must cause a shift in the Schlenk equilibrium producing more of the CH_3MgBr species and decreasing the amount of $(CH_3)_2Mg$. The reaction rate should decrease markedly on addition of magnesium bromide if the reaction of methyl bromide Grignard reagent proceeds to a significant extent through the $(CH_3)_2Mg$ species. If the reaction proceeds predominantly through the CH_3MgBr species, the reaction rate should increase slightly on addition of magnesium bromide. The results of experiments in which magnesium bromide was added to the Grignard reagent are summarized in Table 8. The marked decrease in rate resulting when 10% $MgBr_2$ is added is attributed to the shift in the schlenk equilibrium. The results make it clear that reaction proceeds through both CH_3MgBr and $(CH_3)_2Mg$, and that CH_3MgBr is much less reactive toward benzonitrile than is $(CH_3)_2Mg$.

Several other explanations have been offered for the effect of magnesium bromide on the rate; complexation of magnesium bromide with the Grignard reagent, complexation of magnesium bromide with the organic substrate, and generation of a salt effect. The effect of a Grignard reagent on the solubility of magnesium bromide makes it clear that there is a marked tendency for these two species to associate.[6a] Smith and Su have suggested that a complex between magnesium bromide and CH_3MgBr could have a lower reactivity than the Grignard reagent itself.[26] However, under the conditions employed in the present studies complex formation

between CH_3MgBr and $MgBr_2$ in C_6H_5CN seems unlikely since the maximum concentrations of CH_3MgBr (0.08 M) and $MgBr_2$ (0.027 M) employed are significantly lower than those of Smith and Su (1.4 M and 0.6 M respectively).

To the extent that it is important, $MgBr_2$ would be expected to exhibit a salt effect on the reaction rate by changing the dielectric constant of the Grignard solution. If the salt effect is the major effect when $MgBr_2$ is added, the rate constant should be decreased on adding 20-30% $MgBr_2$ to a comparable degree compared to the large decrease observed on adding the initial 10%. In fact, the rate decrease on adding 20-30% $MgBr_2$ after adding the initial 10% was relatively small (Figure 4). The observed results at 10, 20, and 30% are what would be expected, however, if the principal effect is the shift in the Schlenk equilibrium.

The small decrease in rate occurring in the last three experiments in Table 8 could be attributed to a salt effect. A more satisfactory explanation, however, is based on the assumption that magnesium bromide complexes strongly with the nitrile, thus decreasing the rate by decreasing the amount of nitrile available for reaction.

If these interpretations are correct, the bimolecular rate constant for reaction of RMgX with nitrile must be about 1.0×10^{-3}, and the equilibrium constant for complexation with $MgBr_2$ has a magnitude about 10-12.

Interaction of Benzonitrile and Methylmagnesium Bromide

Complex formation between benzonitrile and organoaluminum compounds has been intensively studied.[28-30] Although the idea of initial

Table 8. Effect of Addition of $MgBr_2$ on the Reaction of Methylmagnesium Bromide With Benzonitrile

Run	$[\text{Methylmagnesium Bromide}]_o$	$[C_6H_5CN]_o \times 10^3$, M	$[MgBr_2]_o \times 10^3$, M	$MgBr_2$ (%)	$k_G \times 10^4$ min^{-1}	$k_G \times 10^4$ min^{-1} (Calc.)
a	0.0283			0	0.682	
29	0.0283	0.993	2.87	10.2	0.279	
30	0.0277	0.970	5.54	20.1	0.285	0.37
b	0.0886			0	2.13	
31	0.0886	1.595	8.95	9.9	0.971	1.14
32	0.0886	1.596	17.8	20.1	0.906	0.97
33	0.0885	1.593	26.9	30.4	0.816	0.90

[a] and [b] data were obtained from the reaction of C_6H_5CN in excess methylmagnesium bromide

$k_G = \frac{k_G}{[G]_o}$ (Ave.) x $[G]_o$.

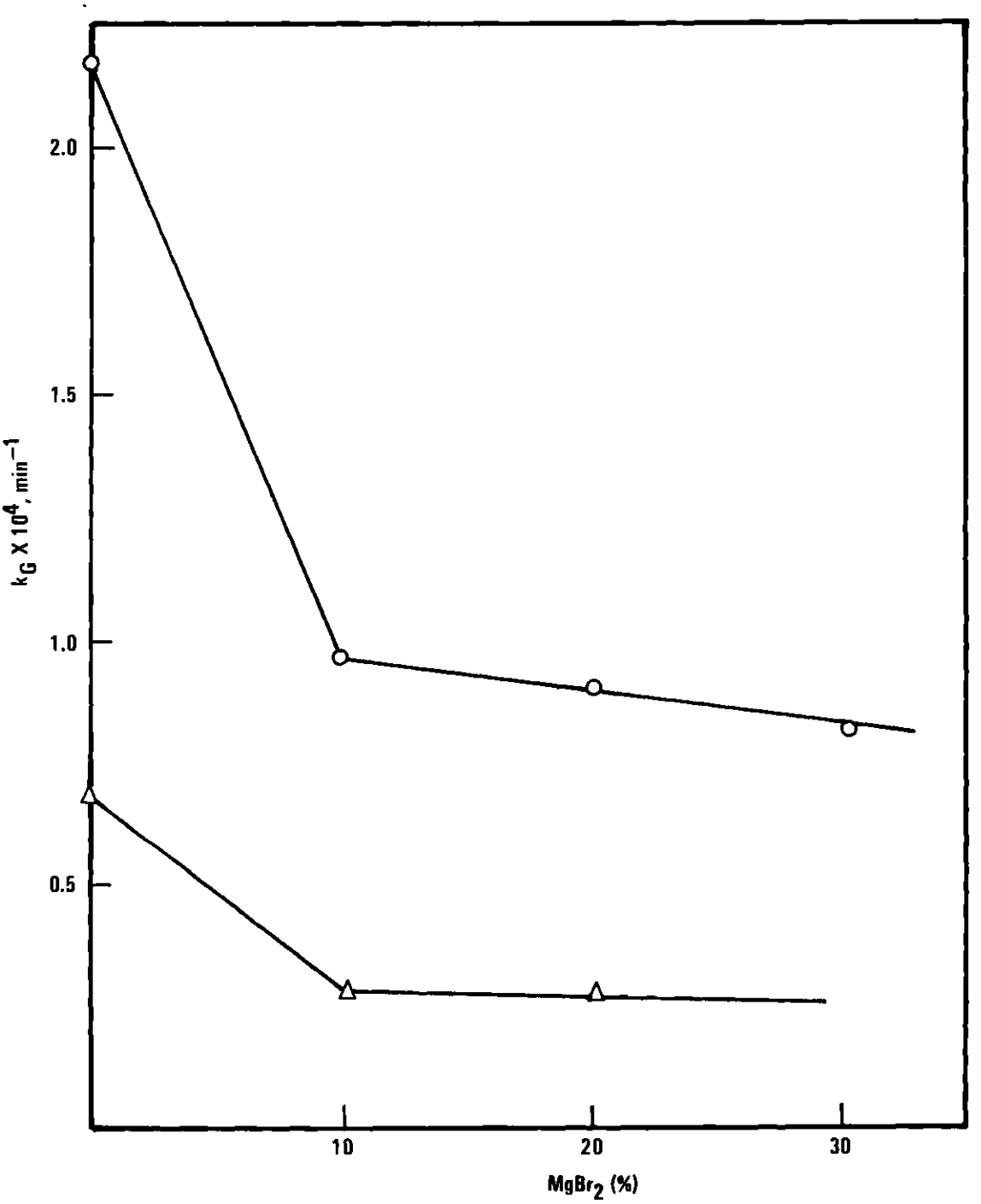


Figure 4. Effect of Addition $MgBr_2$ on the Rate of Reaction of Methylmagnesium Bromide with Benzonitrile:
○, Methylmagnesium Bromide, 8.86×10^{-2} M;
△, Methylmagnesium Bromide, 2.83×10^{-2} M.

complex formation between organomagnesium compounds and ketones seems to be widely accepted, no direct evidence has been presented for complex formation between organomagnesium compounds and benzonitrile. A 1:1 complex between acetonitrile and magnesium bromide in phenetole as solvent has been reported.[31] Vapor pressure lowering was interpreted in terms of a strong 1:1 complex, but the concentrations employed in the experiments were not stated.

In seeking evidence for a complex in our system, methylmagnesium bromide and benzonitrile were mixed in a uv cell. When the concentrations of methylmagnesium bromide and benzonitrile were 1.07×10^{-3} and 9.13×10^{-4}M, respectively, the spectrum of the mixture was the same as the sum of the spectra of the two components. The same was true when the concentrations of methylmagnesium bromide and benzonitrile were 2.56×10^{-3} and 7.99×10^{-3}M, respectively. Thus, there was no evidence of complexation at these concentrations. However, when the concentrations of methylmagnesium bromide and benzonitrile were 8.48×10^{-3} and 9.74×10^{-3}M, the absorption of the mixture in the region 240-285 mμ was distinctly larger than the sum of the components.

Attempts were also made to find evidence for a complex with $MgBr_2$, since $MgBr_2$ is a stronger Lewis acid than CH_3MgBr. The spectrum of a mixture 8.84×10^{-3}M in benzonitrile and 0.119 M in $MgBr_2$ was scanned from 6000 A to 2000 A. The absorption of the mixture in the region 240-265 mμ was somewhat greater than the sum of the components. The observed effect was less than that with the highest concentration of nitrile and Grignard reagent.

In summary, the uv data indicate that complexation does occur with

$MgBr_2$ and CH_3MgBr, but quantitative evaluation of the extent of complexation was not possible.

Evidence for complexation was also sought using infrared spectroscopy. The spectrum of a mixture of CH_3MgBr and C_6H_5CN, each 0.166 M in concentration was scanned from 800 cm^{-1} to 3500 cm^{-1}. In the C_6H_5CN diethyl ether solution the C≡N stretch band appears at 2236 cm^{-1}. A new band was formed after CH_3MgBr and C_6H_5CN were mixed at 1633 cm^{-1} which was attributed to the C=N in the product. The region of the spectrum carefully examined was that portion from 2150 to 2350 cm^{-1}, in which bands due to a complex would be expected. However, no additional band nor any change in the absorption band attributed to C_6H_5CN was observed.

Redistribution of $C_6H_5C(CH_3)NMgCH_3$ and $MgBr_2$

The redistribution of $C_6H_5C(CH_3)NMgCH_3$ and $MgBr_2$ was investigated by simply adding together ether solutions of both components. Both $C_6H_5C(CH_3)NMgCH_3$ and $MgBr_2$ are soluble in diethyl ether; however, $C_6H_5C(CH_3)NMgBr$ is quite insoluble. When equivalent amounts of $C_6H_5C(CH_3)NMgCH_3$ and $MgBr_2$ were mixed, a yellow precipitate formed immediately. Elemental analysis of the dried precipitate showed the Mg:Br ratio to be 1.00:1.09 and the filtrate was identified as CH_3MgBr. Redistribution had occurred to at least 92% completion based on the elemental analysis.

$$C_6H_5-\underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}=N-Mg-CH_3 + MgBr_2 \longrightarrow C_6H_5-\underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}} = N-Mg-Br \downarrow + CH_3MgBr \qquad (11)$$

CHAPTER IV

DISCUSSION

In dealing with reactions of Grignard reagents, the rate law is commonly expressed in terms of the concentration of "Grignard reagent." Thus, to this point we have written the rate law as:

$$\text{Rate} = k[\text{nitrile}][\text{Grignard}] \tag{12}$$

The results reported above suggest that R_2Mg and RMgX each react by separate paths. The reaction rate should then be expressed as:

$$\text{Rate} = k_2[R_2Mg][\text{nitrile}] + k_1[RMgX][\text{nitrile}] \tag{13}$$

The results also suggest that RMgX and MgX_2 form complexes with the nitrile. The overall behavior of the system can then be described by a model similar to that which proved successful for describing the reaction of methylmagnesium bromide with benzophenone.[32] The measured rate constants k_G, k_N and k_{app} can be expressed in terms of the fundamental rate and equilibrium constants of this model. The model was deemed satisfactory if a set of constants could be found which allowed calculation of satisfactory values of the measured rate constants.

The calculations were performed in the following ways:

(1) For experiments in excess Grignard:

$$k_G = \frac{k_1 + k_2\sqrt{(1 + K_3[N])K_s}}{1 + K_1[G]_o + \frac{K_3\sqrt{(1 + K_3[N])K_s[G]_o}}{1 + K_3[N]}} \quad [G]_o \qquad (14)$$

Since [N] is small under these conditions, the approximation [N] =[N]$_o$ was made in this case.

(2) For experiments in excess nitrile:

$$k_N = \frac{k_1 + k_2\sqrt{(1+ K_3[N])K_s}}{1 + k_1[N] + 2\sqrt{(1 + K_3[N])K_s}} \quad [N] \qquad (15)$$

(3) For experiments with low ratio reactants:

$$k_{app} = \frac{k_1 + k_2\sqrt{(1 + K_3[N])K_s}}{1 + K_1[N] + 2\sqrt{(1 + K_3[N])K_s}} \quad \frac{[N]}{[N]_o} \qquad (16)$$

The value of [N] was obtained by successive approximations using the equation

$$[N] = [N]_o - \frac{K_1[N] + K_1K_3[N]^2 + K_3[N]\sqrt{(1 + K_3[N])K_s}}{(1 + K_3[N])(1 + K_1[N] + 2\sqrt{(1 + K_3[N])K_s}} \quad [G]_o \qquad (17)$$

(4) For experiments in excess Grignard with added $MgBr_2$:

$$k_G = \frac{k_1[G]_o + \frac{k_2}{2}\left\{\sqrt{[X]_o^2 + 4K_s[G]_o^2 - 8K_s[G]_o[X]_o} - [X]_o\right\}}{1 + K_1[G]_o + K_3[X]_o} \qquad (18)$$

Calculated values of the measured rate constants are given in all of the

tables for comparison with the measured values. The constants used in the calculations were: $k_1 = 1.3 \times 10^{-3}$ 1 mole^{-1}min^{-1}, $k_2 = 16.3 \times 10^{-3}$ 1 mole^{-1}min^{-1}, $K_1 = 2.3\ M^{-1}$, $K_3 = 10\ M^{-1}$, and $K_s = 0.004$.

Since R_2Mg is an important reactive species in this system, a comment is necessary in relation to the linearity of the pseudo-first-order plots (such as Figure 1) for reactions in excess Grignard, since we have reported curvature in the analogous reaction with benzophenone.[16] A comment is particularly necessary, since the reason for the curvature has apparently been misunderstood.[33]

Equating the expressions

$$\text{Rate} = k[\text{nitrile}][\text{Grignard}] \tag{19}$$

and

$$\text{Rate} = \left(k_2[R_2Mg] + k_1[RMgX]\right)[\text{nitrile}] \tag{20}$$

gives

$$k = k_2 \frac{R_2Mg]}{[\text{Grignard}]} + k_1 \frac{[RMgX]}{[\text{Grignard}]} \tag{21}$$

$$= k_2 F_{R_2Mg} + k_1 F_{RMgX} \tag{22}$$

where F_{R_2Mg} and F_{RMgX} are the fractions of the Grignard reagent that are R_2Mg and RMgX respectively. The pseudo-first-order plots will be strictly linear (and this will hold both for reaction in excess Grignard and in excess nitrile) only if k remains constant during the course of the reaction. The latter depends, in turn, primarily on whether F_{R_2Mg}

remains constant.

The reaction of R_2Mg with C_6H_5CN would be expected to lead to $C_6H_5-\overset{R}{\underset{|}{C}}=N-MgR$ as the initial product. As R_2Mg reacts, it is replenished via the mobile Schlenk equilibrium

$$2\ RMgX \rightleftharpoons R_2Mg + MgX_2 \qquad (23)$$

If these are the only reactions occurring in the system, the concentration of MgX_2 will increase with time, and F_{R_2Mg} will decrease with time rather than remaining constant. It is this mass action effect on the position of equilibrium, rather than any slowness in the rate of formation of R_2Mg,[30] that accounts for curvature in the pseudo-first-order plots.

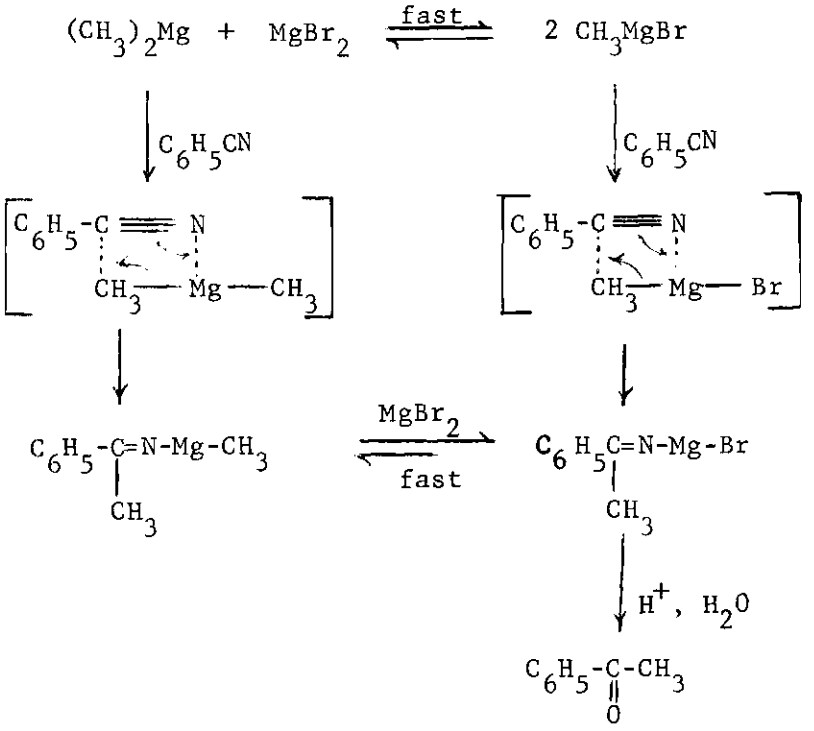
Any redistribution reaction which tends to keep $[R_2Mg]$ and $[MgX_2]$ of equal value, will tend to keep F_{R_2Mg} constant. The reaction is most

$$C_6H_5-\overset{R}{\underset{|}{C}}=N-MgR + MgX_2 \longrightarrow C_6H_5-\overset{R}{\underset{|}{C}}=N-MgX + RMgX \qquad (24)$$

important in this regard. If it is rapid and complete, F_{R_2Mg} will be constant during the reaction. The redistribution reaction was observed to occur within seconds when the reactants were at 0.08 M concentration. The kinetic evidence suggests that redistribution is rapid even at the lower concentrations used in the kinetic experiments. The experiments in excess benzonitrile would be most sensitive to a slow or incomplete redistribution because of the low concentrations of product and Grignard species. The linearity of the pseudo-first-order plots (such as Figure 2), and the agreement of the rate constants so obtained with those obtained

in excess Grignard, provide strong evidence that redistribution is rapid and essentially complete in all of our experiments.

According to all the information presented, the detailed mechanism for the reaction of methylmagnesium bromide with benzonitrile is as follows:



Even though the reaction of methylmagnesium bromide with benzonitrile follows two distinct reaction paths, the reaction kinetically still obeys the simple second-order rate equation.

The Grignard addition reaction was 100% complete when no side reaction occurred. The conclusion that this reaction does not proceed by a free radical mechanism is consistent with the developing idea that single electron transfer participation in Grignard reactions increases

in the order: $CH_3 < i\text{-}C_3H_7 < t\text{-}C_4H_9$.[34]

CHAPTER V

CONCLUSION

The kinetics of the reaction of methylmagnesium bromide with benzonitrile in diethyl ether at 25° was examined in detail in both excess Grignard reagent and excess nitrile. The reaction was found to produce on hydrolysis, the alkylation product acetophenone in quantitative yield when the Grignard reagent was prepared from single crystal magnesium. The kinetic data of the reaction show a second-order reaction, first-order in Grignard reagent and first-order in nitrile. The results of rate studies in the presence of added $MgBr_2$ show that the reaction of the Grignard reagent with benzonitrile occurs through both the $(CH_3)_2Mg$ and CH_3MgBr species. All of the accumulated information is consistent with a mechanism which follows two reaction paths. One path involves reaction of benzonitrile with CH_3MgBr species whereas the other path involves reaction of benzonitrile with $(CH_3)_2Mg$ to form $C_6H_5C(CH_3)NMgCH_3$ which subsequently and rapidly redistributes with $MgBr_2$ to form the final product $C_6H_5C(CH_3)NMgBr$ and methylmagnesium bromide. Evidence for the formation of a complex between nitrile and Grignard species was found when the concentrations of both reactants were greater than 8×10^{-3} M. The detailed mechanism of this reaction is given in equation 25 in the main body of this dissertation.

APPENDIX

Derivation 1. Equation applying to reaction in excess Grignard.

Definitions

$[G]_o$ = Analytical amount of Grignard added at zero reaction time

$[N]_o$ = Analytical amount of nitrile added at zero reaction time

$[M]$ = Total species containing magnesium

$[C_1]$ = Complex between N and CH_3MgBr

$[C_3]$ = Complex between N and $MgBr_2$

$[G]$ = Concentration of CH_3MgBr

$[X]$ = Magnesium bromide concentration

$[R]$ = Concentration of dimethylmagnesium

Equilibrium Conditions

$$2\ CH_3MgBr \rightleftharpoons (CH_3)_2Mg + MgBr_2 \qquad K_s = \frac{[R]\ [X]}{[G]^2}$$

$$CH_3MgBr + N \rightleftharpoons C_1 \qquad K_1 = \frac{[C_1]}{[G]\ [N]}$$

$$MgBr_2 + N \rightleftharpoons C_3 \qquad K_3 = \frac{[C_3]}{[X]\ [N]}$$

Rate Conditions

$$CH_3MgBr + N \xrightarrow{k_1} P_1$$

$$(CH_3)_2Mg + N \xrightarrow{k_2} P_2$$

Derivation

The property being measured is

$$x = [N] + [C_1] + [C_3]$$

$$-\frac{dx}{dt} = k_G x$$

$$= k_1[G][N] + k_2[R][N]$$

$$= \{k_1[G] + k_2[R]\}\ [N]$$

$$K_1 = \frac{[C_1]}{[G][N]} \qquad [C_1] = K_1[G][N]$$

$$K_3 = \frac{[C_3]}{[X][N]} \qquad [C_3] = K_3[X][N]$$

$$x = [N] + [C_1] + [C_3] = [N](1 + K_1[G] + K_3[X])$$

$$[N] = \frac{x}{1 + K_1[G] + K_3[X]}$$

$$k_G x = \{k_1[G] + k_2[R]\} \frac{x}{1 + K_1[G] + K_3[X]}$$

$$k_G = \frac{k_1[G] + k_2[R]}{1 + K_1[G] + K_3[X]}$$

Conservation of Mg:

$$[G]_o = [G] + [C_1] + [R] + [X] + [C_3]$$

Conservation of R:

$$[G]_o = [G] + [C_1] + 2[R]$$

Conservation of X:

$$[G]_\circ = [G] + [C_1] + 2[X] + 2[C_3]$$

$$[R] = [X] + [C_3] = [X] + K_3[X][N]$$

$$= [X](1 + K_3[N])$$

$$[X] = \frac{[R]}{1 + K_3[N]}$$

$$K_s = \frac{[R][X]}{[G]^2} = \frac{[R]^2}{(1 + K_3[N])[G]^2}$$

$$[R]^2 = (1 + K_3[N])K_s[G]^2$$

$$[R] = \sqrt{(1 + K_3[N])K_s}[G]$$

$$[X] = \frac{\sqrt{(1 + K_3[N])K_s}}{1 + K_3[N]} \quad [G]$$

$$[G]_\circ = [G] + K_1[G][N] + \sqrt{(1 + K_3[N])K_s}\ [G] + [X] + K_3[X][N]$$

$$= [G]\{1 + K_1[N] + \sqrt{(1 + K_3[N])K_s}\} + [X](1 + K_3[N])$$

$$= [G]\{1 + K_1[N] + \sqrt{(1 + K_3[N])K_s} + \sqrt{(1 + K_3[N])K_s}\}$$

$$= [G]\{1 + K_1[N] + 2\sqrt{(1 + K_3[N])K_s}\}$$

$$[G] = \frac{[G]_\circ}{1 + K_1[N] + 2\sqrt{(1 + K_3[N])K_s}} = Q[G]_\circ$$

where $$Q = \frac{1}{1 + K_1[N] + 2\sqrt{(1 + K_3[N])K_s}}$$

$$k_G = \frac{k_1[G] + k_2[R]}{1 + K_1[G] + K_3[X]}$$

$$= \frac{k_1[G] + k_2\sqrt{(1 + K_3[N])K_s}\,[G]}{1 + K_1[G] + \frac{K_3\sqrt{(1 + K_3[N])K_s}}{1 + K_3[N]}\,[G]}$$

$$= \frac{k_1 + k_2\sqrt{(1 + K_3[N])K_s}}{1 + K_1[G] + \frac{K_3\sqrt{(1 + K_3[N])K_s}}{1 + K_3[N]}\,[G]}\,[G]$$

$$= \frac{k_1 + k_2\sqrt{(1 + K_3[N])K_s}}{1 + K_1Q[G]_\circ + \frac{K_3\sqrt{(1 + K_3[N])K_s}}{1 + K_3[N]}\,Q[G]_\circ}\,Q[G]_\circ$$

As approximation Q = 1

$$k_G = \frac{k_1 + k_2\sqrt{(1 + K_3[N])K_s}}{1 + K_1[G]_\circ + \frac{K_3\sqrt{(1 + K_3[N])K_s}}{1 + K_3[N]}\,[G]_\circ}\,[G]_\circ$$

Derivation 2. Equation applying to reaction in excess Grignard with added MgX_2.

Because of values of K_1 and K_3 and $[N]_\circ$, no significant fractions of magnesium species are present as complexes.

Conservation of Mg:

$$[G]_o + [X]_o = [G] + [R] + [X]$$

Conservation of X:

$$[G]_o + 2[X]_o = [G] + 2[X]$$

Conservation of R:

$$[G]_o = [G] + 2[R]$$

$$[X]_o = [X] - [R]$$

$$[X] = [X]_o + [R]$$

$$[G]_o = [G] + 2[R]$$

$$[G] = [G]_o - 2[R]$$

$$K_s = \frac{[R][X]}{[G]^2}$$

$$K_s[G]^2 = [R][X]$$

$$K_s\{[G]_o - 2[R]\}^2 = [R]\{[X]_o + [R]\}$$

$$K_s\{[G]_o^2 - 4[R][G]_o + 4[R]^2\} = [R][X]_o + [R]^2$$

$$[R]^2(1 - 4K_s) + ([X]_o + 4K_s[G]_o)[R] - K_s[G]_o^2 = 0$$

$$[R] = \frac{-([X]_o + 4K_s[G]_o) + \sqrt{[X]_o^2 + 4K_s[G]_o^2 - 8K_s[G]_o[X]_o}}{2(1 - 4K_s)}$$

Assume $K_s \ll 1$

$$[R] = \frac{\sqrt{[X]_o^2 + 4K_s[G]_o^2 - 8K_s[G]_o[X]_o} - [X]_o}{2}$$

$$-\frac{d[M]}{dt} = \text{Rate}_{calc.} = k_1[G][N] + k_2[R][N]$$

$$-\frac{d[M]}{dt} \quad \text{Rate}_{meas.} = k_G[N]_{expt.}$$

$$[N]_{expt.} = [N] + [C_1] + [C_3]$$

$$= [N] + K_1[N][G]_o + K_3[N][X]_o$$

$$= [N](1 + K_1[G]_o + K_3[X]_o)$$

$$k_G = \frac{(k_1[G] + k_2[R])[N]}{[N]_{expt.}}$$

$$= \frac{k_1[G]_o + k_2/2\{\sqrt{[X]_o^2 + 4K_s[G]_o^2 - 8K_s[G]_o[X]_o} - [X]_o\}}{1 + K_1[G]_o + K_3[X]_o}$$

Derivation 3. Equation applying to reaction with low ratio reactants.

$$[G]_o = [M] = [R] + [G] + [X] + [C_1] + [C_3]$$

$$[N]_o = [N] + [C_1] + [C_3]$$

$$[R] = [X] + [C_3]$$

$$[R] = \sqrt{(1 + K_3[N])K_s}\ [G]$$

$$[X] = \frac{\sqrt{(1 + K_3[N])K_s}\ [G]}{1 + K_3[N]}$$

$$[G] = \frac{1}{(1 + K_1[N]) + 2\sqrt{(1 + K_3[N])K_s}}\ [M]$$

$$[R] = \frac{\sqrt{(1 + K_3[N])K_s}}{(1 + K_1[N]) + 2\sqrt{(1 + K_3[N])K_s}}\ [M]$$

$$-\frac{d[M]}{dt} = \text{Rate}_{\text{calc.}} = k_1[G][N] + k_2[R][N]$$

$$-\frac{d[M]}{dt} = \text{Rate}_{\text{meas.}} = k_{\text{app.}}[G]_\circ [N]_\circ$$

$$k_{\text{app.}} = \frac{k_1[G][N] + k_2[R][N]}{[G]_\circ[N]_\circ}$$

$$= k_1 \frac{[G][N]}{[G]_\circ[N]_\circ} + k_2 \frac{[R][N]}{[G]_\circ [N]_\circ}$$

$$= \frac{k_1}{(1 + K_1[N] + 2\sqrt{(1 + K_3[N])K_s}} \frac{[N]}{[N]_\circ} +$$

$$\frac{k_2\sqrt{(1 + K_3[N])K_s}}{(1 + K_1[N] + 2\sqrt{(1 + K_3[N])K_s}} \frac{[N]}{[N]_\circ}$$

$$= \frac{k_1 + k_2\sqrt{(1 + K_3[N])K_s}}{1 + K_1[N] + 2\sqrt{(1 + K_3[N])K_s}} \frac{[N]}{[N]_\circ}$$

Derivation for [N] calculation

$$[N]_o - [N] = [C_1] + [C_3] = K_1[G][N] + K_3[X][N]$$

$$= \frac{K_1[N]}{(1 + K_1[N]) + 2\sqrt{(1 + K_3[N])K_s}}[M]$$

$$+ \frac{K_3[N]\sqrt{(1 + K_3[N])K_s}}{1 + K_3[N]} \cdot$$

$$\frac{1}{(1 + K_1[N]) + 2\sqrt{(1 + K_3[N])K_s}}[M]$$

$$[N] = [N]_o - \frac{K_1[N] + K_1K_3[N]^2 + K_3[N]\sqrt{(1 + K_3[N])K_s}}{(1 + K_3[N])\{(1 + K_1[N]) + 2\sqrt{(1 + K_3[N])K_s}\}}[M]$$

$$= [N]_o - \frac{K_1[N] + K_1K_3[N]^2 + K_3[N]\sqrt{(1 + K_3[N])K_s}}{(1 + K_3[N])\{(1 + K_1[N]) + 2\sqrt{(1 + K_3[N])K_s}\}}[G]_o$$

Derivation 4. Equation applying to reaction in excess benzonitrile.

$$-\frac{d[M]}{dt} = \text{Rate}_{\text{calc.}} = k_1[G][N] + k_2[R][N]$$

$$-\frac{d[M]}{dt} = \text{Rate}_{\text{meas.}} = k_N[G]_o$$

$$k_N = \frac{k_1[G][N] + k_2[R][N]}{[G]_o}$$

Similar to derivation 3

$$k_N = \frac{k_1 + k_2 \sqrt{(1 + K_3[N])K_s}}{1 + K_1[N] + 2\sqrt{(1 + K_3[N])K_s}} [N]$$

Table 9. Reaction of Benzonitrile with Excess Methylmagnesium Bromide at 25° (Run 1 and 2)

Time min	Reaction (%)	$k_G \times 10^4$ min^{-1}	Time min	Reaction (%)	$k_G \times 10^4$ min^{-1}
596	11.03		594	8.59	
1189	18.46		1185	16.26	
2114	27.03	1.491	2113	25.39	1.386
2667	31.32	1.409	2663	31.65	1.429
3550	34.52	1.193	3548	38.70	1.379
4252	45.52	1.428	4248	45.96	1.449
5264	52.63	1.419	5263	56.84	
6413	57.77	1.344	6409	57.78	1.345
7263	65.94	1.483	7261	62.99	1.369
9291	73.17	1.416	9290	70.84	1.327
10759	77.78	1.398	10755	74.64	1.276
		Ave. 1.398 ± 0.057			Ave. 1.370 ± 0.041

$[N]_o = 5.90 \times 10^{-4}$ M

$[G]_o = 5.82 \times 10^{-2}$ M

$k_G^* = 1.41 \times 10^{-4}$ min^{-1}

$[N]_o = 10.07 \times 10^{-4}$ M

$[G]_o = 5.82 \times 10^{-2}$ M

$k_G^* = 1.39 \times 10^{-4}$ min^{-1}

*Observed rate constant was made a correction on volume change which is due to different addition of nitrile solution.

Table 10. Reaction of Benzonitrile with Excess Methylmagnesium Bromide at 25° (Run 3 and 4)

Time min	Reaction (%)	$k_G \times 10^4$ min^{-1}	Time min	Reaction (%)	$k_G \times 10^4$ min^{-1}
594	9.64		593	8.01	1.408
1182	14.31	1.307	1178	14.96	1.376
2111	26.29	1.445	2110	24.97	1.362
2661	30.74	1.380	2657	30.21	1.354
3545	40.06	1.444	3545	36.56	1.284
4245	42.94	1.322	4241	42.49	1.304
5260	51.48	1.262	5260	47.18	1.213
6406	55.19	1.253	6402	54.69	1.237
7261	60.84	1.291	7259	55.50	
9289	71.89	1.366	9294	67.41	1.206
10752	71.98		10748	72.81	1.212
		Ave. 1.341 ± 0.060			Ave. 1.296 ± 0.065

$[N]_o = 1.378 \times 10^{-3}$ M $[N]_o = 1.748 \times 10^{-3}$ M

$[G]_o = 5.82 \times 10^{-2}$ M $[G]_o = 5.82 \times 10^{-2}$ M

$k_G^* = 1.36 \times 10^{-4}$ min^{-1} $k_G^* = 1.32 \times 10^{-4}$ min^{-1}

*Observed rate constant was made a correction on volume change which is due to different addition of nitrile solution.

Table 11. Reaction of Benzonitrile with Excess Methylmagnesium Bromide at 25° (Run 5 and 6)

Time min	Reaction (%)	$k_G \times 10^4$ min^{-1}	Time min	Reaction (%)	$k_G \times 10^4$ min^{-1}
1163	9.24		1397	8.02	
2733	13.33	0.5235	2460	17.11	0.7628
3794	18.72	0.5463	3348	21.41	0.7196
4685	24.76		4792	29.16	0.7194
6128	28.17	0.5399	5934	35.19	0.7283
7270	32.17	0.5339	7084	36.23	
8420	36.86	0.5461	8940	45.54	0.6798
10273	41.54	0.5226	10196	50.40	0.6877
12982	49.17	0.5212	11916	55.83	0.6857
14136	52.96	0.5335	12800	61.24	0.7405
		Ave. 0.5334 ± 0.0082			Ave. 0.7154 ± 0.0233

$[N]_o = 6.00 \times 10^{-4}$ M $\quad$ $[N]_o = 1.49 \times 10^{-3}$ M

$[G]_o = 2.19 \times 10^{-2}$ M $\quad$ $[G]_o = 2.98 \times 10^{-2}$ M

Table 12. Reaction of Benzonitrile with Excess Methylmagnesium Bromide at 25° (Run 7 and 8)

Time min	Reaction (%)	$k_G \times 10^4$ min^{-1}	Time min	Reaction (%)	$k_G \times 10^4$ min^{-1}
435	7.74		582	9.78	
1096	11.96	1.162	1122	15.99	
2525	23.90	1.082	1977	25.24	1.471
4100	38.24	1.175	2701	33.04	1.486
5575	46.30	1.115	3453	39.14	1.438
6665	52.97	1.132	3970	42.63	1.400
7670	57.35	1.111	4929	50.97	1.446
8950	64.20	1.148	6009	58.28	1.455
10210	68.50	1.131	8240	71.19	
			12134	82.12	1.419
		Ave. 1.132 ± 0.022			Ave. 1.445 ± 0.022

$[N]_o = 1.49 \times 10^{-3}$ M $\quad$ $[N]_o = 1.49 \times 10^{-3}$ M

$[G]_o = 4.63 \times 10^{-2}$ M $\quad$ $[G]_o = 5.67 \times 10^{-2}$ M

Table 13. Reaction of Benzonitrile with Excess Methylmagnesium Bromide at 25° (Run 9 and 10)

Time min	Reaction (%)	$k_G \times 10^4$ min^{-1}	Time min	Reaction (%)	$k_G \times 10^4$ min^{-1}
381	7.10		388	8.26	
1104	17.22	1.712	949	18.19	2.116
1621	23.42	1.646	1352	23.63	1.994
2183	30.28	1.652	1927	31.02	1.927
2583	35.48	1.696	2427	39.49	2.070
3161	38.94	1.561	2827	40.07	1.811
4060	48.47	1.633	3290	46.03	1.875
5116	56.23	1.615	4661	59.47	1.938
6561	66.67	1.675	5327	62.37	1.835
9787	81.08	1.701	6526	71.82	1.941
			8556	81.41	1.967
		Ave. 1.655 ± 0.037			Ave. 1.948 ± 0.079

$[N]_o = 1.49 \times 10^{-3}$ M $\quad$ $[N]_o = 1.49 \times 10^{-3}$ M

$[G]_o = 6.80 \times 10^{-2}$ M $\quad$ $[G]_o = 8.44 \times 10^{-2}$ M

Table 14. Reaction of Benzonitrile with Excess Methylmagnesium Bromide at 25° (Run 11)

Time, minutes	Reaction (%)	$k_G \times 10^4$, min^{-1}
518	14.96	
923	21.58	
1496	31.67	2.546
1996	36.91	2.308
2396	42.11	2.281
2861	48.26	2.303
3453	53.09	2.192
4234	61.02	2.225
4896	67.07	2.269
6301	76.50	2.298
8127	84.51	2.295
		Ave. 2.302 ± 0.062

$[N]_o = 1.49 \times 10^{-3}$ M

$[G]_o = 9.98 \times 10^{-2}$ M

Table 15. Reaction of Methylmagnesium Bromide with Excess Benzonitrile at 25° (Run 12)

Time, minutes	Absorbance	Time, minutes	Absorbance
316	0.042	9803	0.232
945	0.064	11019	0.247
1262	0.069	12076	0.250
1784	0.088	12804	0.263
2486	0.106	13236	0.266
2963	0.117	13852	0.273
3708	0.128	14256	0.273
3939	0.135	15529	0.283
4593	0.140	16682	0.297
5199	0.160	17550	0.297
6325	0.185	18299	0.303
6835	0.192	20160	0.315
7584	0.202	21141	0.319
8017	0.208	22707	0.324
8475	0.213	23277	0.317
9505	0.225	26136	0.434

Extrapolated Final Absorbance = 0.285

$[N]_o = 0.0637$ M

$[G]_o = 2.92 \times 10^{-3}$ M

Table 16. Reaction of Methylmagnesium Bromide with Excess Benzonitrile at 25° (Run 13)

Time, minutes	Absorbance	Time, minutes	Absorbance
313	0.047	9801	0.253
944	0.074	11018	0.267
1260	0.081	12080	0.270
1784	0.104	12802	0.281
2485	0.124	13234	0.284
2960	0.139	13852	0.289
3704	0.159	14255	0.290
3938	0.156	16690	0.300
4592	0.163	17548	0.307
5195	0.187	18298	0.310
6324	0.204	19615	0.307
6835	0.215	20159	0.302
7582	0.227	21139	0.340
8014	0.234	22706	0.521
8477	0.238	23993	0.813
9502	0.251	26856	2.293

Extrapolated Final Absorbance = 0.300

$[N]_o = 0.0729$ M

$[G]_o = 2.87 \times 10^{-3}$ M

Table 17. Reaction of Methylmagnesium Bromide with Excess Benzonitrile at 25° (Run 14)

Time, minutes	Absorbance	Time, minutes	Absorbance
3	0.038	10048	0.277
292	0.053	10512	0.279
772	0.070	11538	0.287
1064	0.087	13054	0.293
1617	0.111	14112	0.290
2342	0.137	14840	0.295
2980	0.156	15269	0.295
3297	0.162	15890	0.294
3820	0.178	17566	0.312
4522	0.196	18721	0.372
4998	0.207	19587	0.450
5743	0.218	20336	0.550
7234	0.244	21653	0.799
8359	0.258	22197	0.940
8870	0.264	23178	1.229
9619	0.273	24745	1.810

Extrapolated Final Absorbance = 0.295

$[N]_o = 0.0780$ M

$[G]_o = 2.92 \times 10^{-3}$ M

Table 18. Reaction of Methylmagnesium Bromide with Excess Benzonitrile at 25° (Run 15)

Time, minutes	Absorbance	Time, minutes	Absorbance
233	0.123	6163	0.559
446	0.165	6594	0.558
841	0.214	7305	0.579
1384	0.268	8163	0.600
1718	0.302	3888	0.612
1958	0.321	9665	0.625
2338	0.354	10120	0.639
2924	0.393	10831	0.680
3164	0.413	11482	0.712
3793	0.442	12616	0.785
4383	0.480	13283	0.844
4730	0.500	13895	0.920
5142	0.517	14370	1.003
5895	0.549	18243	2.369

Extrapolated Final Absorbance = 0.625

$[N]_o = 0.101$ M

$[G]_o = 4.33 \times 10^{-3}$ M

Table 19. Reaction of Methylmagnesium Bromide with Excess Benzonitrile at 25° (Run 16)

Time, minutes	Absorbance	Time, minutes	Absorbance
1272	0.128	8429	0.265
1552	0.134	9246	0.274
1952	0.147	9861	0.279
2678	0.171	10185	0.273
2948	0.179	10588	0.279
3526	0.195	11244	0.281
4160	0.209	12706	0.281
4618	0.218	13592	0.288
5483	0.235	15083	0.319
5818	0.240	16282	0.371
6360	0.249	17024	0.433
6844	0.252	18435	0.604
7216	0.257	19738	0.793

Extrapolated Final Absorbance = 0.279

$[N]_o = 0.128$ M

$[G]_o = 3.33 \times 10^{-3}$ M

Table 20. Reaction of Methylmagnesium Bromide with Excess Benzonitrile at 25° (Run 17)

Time, minutes	Absorbance	Time, minutes	Absorbance
590	0.145	6841	0.326
1260	0.143	7214	0.333
1541	0.155	8439	0.350
1941	0.175	9254	0.364
2674	0.210	9868	0.369
2947	0.221	10194	0.367
3525	0.243	10597	0.373
4159	0.262	11253	0.377
4616	0.275	11988	0.381
5483	0.300	12881	0.385
5817	0.307	14373	0.391
6359	0.319		

Extrapolated Final Absorbance = 0.369

$[N]_o$ = 0.128 M

$[G]_o = 4.07 \times 10^{-3}$ M

Table 21. Reaction of Methylmagnesium Bromide with Excess Benzonitrile at 25° (Run 18)

Time, minutes	Absorbance	Time, minutes	Absorbance
1110	0.181	6257	0.329
1711	0.196	6554	0.332
2028	0.202	6907	0.339
2398	0.220	7560	0.350
2660	0.234	8435	0.356
3284	0.258	9768	0.368
3599	0.270	11874	0.377
4157	0.289	12503	0.390
4658	0.303	13333	0.409
5075	0.301	13510	0.414
5599	0.314		

Extrapolated Final Absorbance = 0.370

$[N]_o = 0.127$ M

$[G]_o = 4.67 \times 10^{-3}$ M

Table 22. Reaction of Methylmagnesium Bromide with Excess Benzonitrile at 25° (Run 19)

Time, minutes	Absorbance	Time, minutes	Absorbance
399	0.220	5600	0.692
1102	0.348	6255	0.714
1708	0.426	6554	0.722
2020	0.458	6907	0.733
2393	0.494	7560	0.754
2659	0.523	8435	0.767
3279	0.572	9767	0.786
3598	0.592	11874	0.867
4157	0.630	12504	0.927
4657	0.657	13333	0.996
5075	0.662		

Extrapolated Final Absorbance = 0.785

$[N]_o = 0.127$ M

$[G]_o = 5.94 \times 10^{-3}$ M

Table 23. Reaction of Methylmagnesium Bromide with Excess Benzonitrile at 25° (Run 20)

Time, minutes	Absorbance	Time, minutes	Absorbance
7	0.057	5742	0.300
488	0.145	6282	0.314
1019	0.158	7209	0.318
1579	0.189	8028	0.326
2383	0.222	12820	0.767
3950	0.269	15028	1.536
5007	0.296		

Extrapolated Final Absorbance = 0.325

$[N]_o = 0.150$ M

$[G]_o = 2.01 \times 10^{-3}$ M

Table 24. Reaction of Methylmagnesium Bromide with Excess Benzonitrile at 25° (Run 21)

Time, minutes	Absorbance	Time, minutes	Absorbance
854	0.206	4846	0.434
1464	0.258	5056	0.432
1792	0.287	5819	0.460
2322	0.323	6062	0.455
2893	0.354	6205	0.457
3141	0.361	6559	0.464
3366	0.372	7263	0.461
4336	0.419	9262	0.501
4446	0.419	10109	0.592
4622	0.423		

Extrapolated Final Absorbance = 0.464

$[N]_o = 0.230$ M

$[G]_o = 3.93 \times 10^{-3}$ M

Table 25. Reaction of Methylmagnesium Bromide with Excess Benzonitrile at 25° (Run 22)

Time, minutes	Absorbance	Time, minutes	Absorbance
66	0.172	2555	0.581
235	0.331	2929	0.592
408	0.312	3241	0.601
518	0.335	3952	0.634
1008	0.441	4222	0.663
1123	0.460	4454	0.696
1226	0.480	4834	0.755
1408	0.501	5444	0.910
1707	0.534	5777	1.033
1987	0.551		

Extrapolated Final Absorbance = 0.634

$[N]_o = 0.459$ M

$[G]_o = 3.93 \times 10^{-3}$ M

Table 26. Reaction of Methylmagnesium Bromide with Excess Benzonitrile at 25° (Run 23)

Time, minutes	Absorbance	Time, minutes	Absorbance
181	0.241	1753	0.726
236	0.274	1889	0.743
288	0.303	2247	0.800
337	0.331	2860	0.893
392	0.355	3318	0.947
454	0.385	3791	1.000
611	0.448	4540	1.048
701	0.484	5118	1.080
781	0.515	5678	1.149
843	0.533	6009	1.199
941	0.563	6417	1.285
1333	0.668	7149	1.517
1592	0.711	7526	1.692

Extrapolated Final Absorbance = 1.050

$[N]_o = 0.640$ M

$[G]_o = 3.93 \times 10^{-3}$ M

Table 27. Reaction of Methylmagnesium Bromide with Excess Benzonitrile at 25° (Run 24)

Time, minutes	Absorbance	Time, minutes	Absorbance
189	0.426	1486	0.980
241	0.464	1592	1.009
285	0.500	1749	1.043
336	0.546	1887	1.067
390	0.579	2044	1.091
455	0.613	2248	1.109
611	0.695	2853	1.177
702	0.744	3313	1.267
781	0.769	3790	1.420
843	9.795	4537	1.805
941	0.826	5118	2.260
1328	0.943	5677	2.800
1384	0.960		

Extrapolated Final Absorbance = 1.200

$[N]_o = 0.822$ N

$[G]_o = 3.93 \times 10^{-3}$ M

Table 28. Reaction of Benzonitrile with Methylmagnesium Bromide at 25° (Run 25 and 26)

Time min	Reaction (%)	k_{app}* x 10^3 l. mole^{-1} min^{-1}	Time min	Reaction (%)	k_{app}* x 10^3 l. mole^{-1} min^{-1}
1115	20.85	1.700	1116	15.51	1.753
2363	38.56	1.711	2361	29.43	1.759
3853	53.78	1.698	3854	41.72	1.714
4438	57.60	1.649	4439	45.00	1.660
5625	64.62	1.594	5625	52.17	1.643
7164	76.25	1.770	7165	62.60	1.769
8302	79.94	1.720	8302	68.68	1.834
9386	86.13	1.900	11265	80.70	1.996
			13935	86.48	2.009
$[N]_o$ = 0.02667 M			$[N]_o$ = 0.02897 M		
$[G]_o$ = 0.1262 M			$[G]_o$ = 0.0885 M		

*Calculated from Equation (10)

Table 29. Reaction of Benzonitrile with Methylmagnesium Bromide at 25° (Run 27 and 28).

Time min	Reaction (%)	k_{app}* x 10^3 l. $mole^{-1}$ min^{-1}	Time min	Reaction (%)	k_{app}* x 10^3 l. $mole^{-1}$ min^{-1}
1165	10.86	1.620	2065	7.27	1.408
2596	22.16	1.635	4269	14.15	1.445
3839	30.76	1.666	5807	17.49	1.375
5334	37.70	1.580	8042	23.29	1.438
7105	48.77	1.745	10008	27.24	1.438
8645	52.90	1.642	12487	33.20	1.555
10867	61.95	1.743	15010	38.65	1.669
14559	78.78	1.918	18549	46.51	1.928
16776	80.35	2.109			
	$[N]_o$ = 0.03092 M			$[N]_o$ = 0.03375 M	
	$[G]_o$ = 0.0627 M			$[G]_o$ = 0.0272 M	

*Calculated from Equation (10)

Table 30. Reaction of Methylmagnesium Bromide with Benzonitrile in the Presence of Magnesium Bromide at 25° (Run 29 and 30)

Time min	Reaction (%)	$k_G \times 10^4$ min^{-1}	Time min	Reaction (%)	$k_G \times 10^4$ min^{-1}
1484	2.35	0.1603	4694	9.63	
10934	29.70	0.3223	6148	16.44	0.2921
16079	35.08	0.2687	7637	22.22	0.3123
26555	49.92	0.2604	10931	28.02	0.3008
30713	56.42	0.2704	16075	35.22	0.2701
37407	64.02	0.2733	20625	45.04	0.2902
		Ave. 0.2790 $\pm$ 0.0178	26551	51.96	0.2761
			30714	57.50	0.2786
			37407	62.65	0.2633
					Ave. 0.2854 $\pm$ 0.0134

$[N]_o = 9.93 \times 10^{-4}$ M
$[G]_o = 2.83 \times 10^{-2}$ M
$[MgBr_2]_o = 2.87 \times 10^{-2}$ M

$[N]_o = 9.70 \times 10^{-4}$ M
$[G]_o = 2.77 \times 10^{-2}$ M
$[MgBr_2]_o = 5.54 \times 10^{-3}$ M

Table 31. Reaction of Methylmagnesium Bromide with Benzonitrile in the Presence of Magnesium Bromide at 25 ° (Run 31 and 32)

Time min	Reaction (%)	$k_G \times 10^4$ min^{-1}	Time min	Reaction (%)	$k_G \times 10^{-4}$ min^{-1}
1564	10.56		1563	14.99	
3691	29.19	0.9352	3688	26.62	0.8393
5111	35.14		5110	36.89	0.9008
8027	53.96	0.9663	8024	51.96	0.9137
10951	65.98	0.9846	10950	62.35	0.8921
13334	72.84	0.9775	13334	70.23	0.9087
15852	79.33	0.9945	15851	76.94	0.9255
19391	84.72	0.9688	19390	84.46	0.9602
		Ave. 0.9712 $\pm$ 0.0144			Ave. 0.9058 $\pm$ 0.0243
$[N]_o = 1.595 \times 10^{-3}$ M			$[N]_o = 1.596 \times 10^{-3}$ M		
$[G]_o = 8.86 \times 10^{-2}$ M			$[G]_o = 8.86 \times 10^{-2}$ M		
$[MgBr_2]_o = 8.95 \times 10^{-3}$ M			$[MgBr_2]_o = 1.78 \times 10^{-2}$ M		

Table 32. Reaction of Methylmagnesium Bromide with Benzonitrile in the Presence of Magnesium Bromide at 25° (Run 33)

Time, minutes	Reaction (%)	$k_G \times 10^4$, min^{-1}
1563	6.02	
3684	24.94	0.7787
5109	31.79	0.7488
8882	53.15	0.8537
13432	67.10	0.8276
15851	73.69	0.8424
19389	80.56	0.8447
		Ave. 0.8160 ± 0.0348

$[N]_o = 1.593 \times 10^{-3}$ M

$[G]_o = 8.85 \times 10^{-2}$ M

$[MgBr_2]_o = 2.69 \times 10^{-2}$ M

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PART II

THE MECHANISM OF DIMETHYLMAGNESIUM ADDITION TO BENZONITRILE

CHAPTER I

INTRODUCTION

Background

The composition of dimethylmagnesium in diethyl ether is simpler than that of the methyl bromide Grignard. Dimethylmagnesium is predominantly monomeric in diethyl ether at low concentration, however, association takes place at concentrations greater than 0.1m. Dimeric association is approached (i=2) only at concentrations greater than 1m.[1,2]

Little data is available concerning the reactions of dialkylmagnesium compounds with nitriles in diethyl ether. Becker[3] has reported that diethylmagnesium in THF reacts with benzonitrile, however, only 50% of the ethyl groups participated in the reaction and the remaining groups failed to give a positive Gilman test. In addition, Becker reported two distinct rates of reaction. Since dialkylmagnesium compounds make a contribution to the total description of the Grignard reagent and contribute to the total rate of the reaction of Grignard reagents with nitrile, it is important to have an understanding of the kinetics of the reaction of a typical dialkylmagnesium with a representative nitrile. A kinetic study of the reaction of dimethylmagnesium with benzonitrile, parallel to that conducted with the Grignard reagent, was carried out in the hope that the results would be consistent with the results already obtained from the previous study.

Benzonitrile and dimethylmagnesium were chosen as reactants in order to eliminate certain side reactions known to occur with other

nitriles and other organomagnesium compounds. Since no α-hydrogen exists on benzonitrile, enolization cannot occur as a side reaction and since no β-hydrogen exists on dimethylmagnesium, reduction cannot occur as a side reaction. The sole, or at least major, product expected is $C_6H_5C(CH_3)NMgCH_3$, arising from the addition reaction.

Purpose

The kinetics of the reaction of benzonitrile with dimethylmagnesium diethyl ether solution was carried out in an attempt to establish the mechanism of this reaction.

CHAPTER II

EXPERIMENTAL

Chemicals

Single crystal magnesium[4] from Ventron Corporation was used. Eastman spectro grade benzonitrile[4] was used and distilled under vacuum over solid methylmagnesium bromide. N-tetradecane (Chemical Samples, 99.9% purity) was dried and distilled at 55° and 0.02 mm pressure from Linde 4A molecular sieves. It was used as the internal standard in the kinetic studies. Acetophenone (Eastman) was distilled from a spinning band distillation column under vacuum. It was as a standard to identify the reaction product. Dimethylmercury (Strem Chemicals) was used without further purification. Diethyl ether (Fisher Anhydrous) was distilled under nitrogen from $LiAlH_4$ through a 60cm distilling column packed with glass rings.

The Preparation of Dimethylmagnesium

Dimethylmagnesium was prepared by allowing an excess of magnesium turnings (2.7 g, 0.11 g-atom) to stir slowly overnight with dimethyl mercury (5.9 ml, 0.075 mole) in the dry box. The resulting dimethylmagnesium was extracted with diethyl ether and stored in a glass flask equipped with a three-way teflon stopcock. Diethyl ether solutions of $(CH_3)_2Mg$ are clear and colorless. The analysis of dimethylmagnesium was carried out by both the Gilman and EDTA methods and gave a C-Mg/Mg ratio of 2.006:1.000. Thioacetamide test for ionic Hg on hydrolyzed samples of $(CH_3)_2Mg$ was negative.

Instrumentation and Apparatus

An inert atmosphere box (Kewaunee Model 2C1020) equipped with a recirculating system[5] to remove moisture and oxygen was used during the manipulation of air-sensitive reagents. As an added precaution, a special line of prepurified nitrogen was available in the glove box in order that all materials could be transferred in Schlenk tubes under a blanket of prepurified nitrogen.[6]

A F & M Model 700 flame ionization gas chromatograph equipped with dual six foot one-eight inch stainless steel 10% FFAP columns was used to analyze the products.

All visible and ultraviolet spectra were recorded on a Cary Model 14 recording spectrophotometer. A Zeiss PMQ II single beam spectrophotometer was employed for making absorbance measurements for the kinetic studies.

Matched quartz cells (Beckman, 10.0 mm) equipped with a 1 mm bore two-way Kimax micro teflon stopcock and Zeiss, 1.00 mm cells were used for all ultraviolet measurements.

A Sargent constant temperature water bath was used for controlling the temperature (±0.02° C) of the kinetic solutions, temperatures were monitored with a calibrated thermometer reading to 0.1° with estimates to 0.02° possible.

Reactions were timed with a Rolex precision watch.

The kinetic flasks were fabricated by sealing a three-way teflon stopcock to the top of a 100 ml heavy walled glass bulb.

The syringes employed for transfer of the samples were calibrated with stainless steel needles. Deliveries could be reproduced to better

than $\pm$ 0.5%.

NMR Techniques

Variable temperature nmr spectra were obtained using a Jeol 100-MHz nmr spectrometer.[2] The materials to be studied were taken into the dry box and samples were transferred by means of a syringe into an nmr tube which had been fitted with a thick-walled adaptor for sealing. TMS was usually added and a three-ring cap used for a temporary seal. Silicone grease was applied around the bottom of the cap before removing the tube from the dry box, freezing in liquid nitrogen, and sealing with a torch.

Analyses

All solutions were analyzed for magnesium by titration with EDTA; the concentration of basic-magnesium bonded to carbon was determined by adding a known excess amount of acid and back-titration with standard base using phenolphthalein as an indicator (Gilman titration).

Glpc analyses were performed using 6-ft matched stainless steel columns of 10% FFAP on 80-100 mesh Diatoport S. Product yields were determined by comparison of reaction mixtrues with the internal standard, n-tetradecane. The reaction product was identified by comparing the retention time with that of an authentic sample under the conditions of flow rate, 40 ml/min; injection temperature, 230 °C and detector temperature, 230°C; the retention times for n-tetradecane, benzonitrile and acetophenone are 6, 18 and 23 minutes at an oven temperature of 105°C. The reaction mixtures could be satisfactorily separated under this condition.

These different solutions containing known amounts of n-tetradecane, benzonitrile and acetophenone were prepared in diethyl ether and subjected to gas chromatography to give the relationship, (mole nitrile)/(mole n-tetradecane) = 1.95 (area nitrile)/(area n-tetradecane) and (mole nitrile)/(mole ketone) = 1.048 (area nitrile)/(area ketone).

Product Yield Study

Previous workers[3] have said that only 50% of the alkyl groups is available for alkylation. Because of the importance of this point, benzonitrile and $(CH_3)_2Mg$ were allowed to react in diethyl ether in 2:1 and 1:1 ratios. A 1:1 mole ratio mixture of benzonitrile and dimethylmagnesium was prepared by mixing 50 ml of an ether solution of benzonitrile(8.5629g, 8.304×10^{-2}mole) with 158 ml of a 0.5249 M solution of $(CH_3)_2Mg$. Reaction proceeded rapidly to produce the alkylation product in 100% yield within 7 hrs. Two experiments were performed at 2:1 mole ratio of benzonitrile to $(CH_3)_2Mg$. When an 85 ml Et_2O solution of benzonitrile (1.666g, 1.616×10^{-2} mole) and 15.4 ml of 0.5249 M, solution of $(CH_3)_2Mg$ were allowed to react for 80 hrs., alkylation product was formed in 78% yield. After 25 days no reactant remained. In a second experiment 1 ml of benzonitrile (2.822 M) and 2 ml of $(CH_3)_2Mg$ (0.6798 M) were added to 70 ml of diethyl ether. This solution was allowed to react at room temperature for 17 days. Analysis of the mixture, after hydrolysis, with an internal standard present to provide a material balance, gave 90.3% acetophenone and 7.1% benzonitrile.

Kinetic studies were carried out both in excess dimethylmagnesium and in excess benzonitrile. The procedures for the studies in excess dimethylmagnesium were the same as those in excess Grignard reagent.[4]

Kinetic studies in excess benzonitrile were performed in the following fashion. Quartz 10 mm UV cells, glass sealed with 1 mm bore two-way Kimax teflon stopcock, were dried for a few seconds by heating, and then transferred to the dry box. The syringes with stainless steel needles, 25 ml volumetric flasks sealed with a three-way teflon stopcock and other glassware were transferred to the dry box by the routine procedures. The 25 ml flasks and UV cells were purged with prepurified nitrogen via a needle before loading the samples. The desired amounts of standard benzonitrile solution and n-tetradecane, internal standard, were added under nitrogen flow to the 25 ml volumetric flask which was subsequently diluted to the mark with diethyl ether. The certain amount of standard dimethylmagnesium solution was added to the 25 ml volumetric flask. The flask was rapidly shaken to insure mixing. A 4 ml portion of reaction mixture was immediately transferred from the volumetric flask to the UV cell via a calibrated syringe. The UV cell and volumetric flask were removed from the dry box as quickly as possible. The UV cell was placed in the constant temperature compartment of the Zeiss spectrophotometer. The volumetric flask was placed in a constant temperature water bath. At various time intervals samples, generally 8 to 10 in number, were withdrawn from the volumetric flask and quenched in saturated ammonium chloride solution. The quenched reaction mixtures were analyzed for acetophenone by gas chromatography. Simultaneously, 10 sets of time-absorbance values were taken in each kinetic experiemnt by UV.

Fractional Crystallization of the Reaction Product of Dimethylmagnesium Addition to Benzonitrile in Diethyl Ether

Dimethylmagnesium (196 ml, 0.615M solution in diethyl ether), which was prepared from methylmagnesium bromide by the dioxane precipitation method, was transferred to 1000 ml one-neck round-bottom flask containing a large stirring bar. A 400 ml portion of a dilute benzonitrile (12.42 g, 0.121 mole) solution in diethyl ether was added to the dimethylmagnesium solution in the dry box. Then the reaction flask was removed from the dry box and equipped with a Dry Ice condenser to which was attached a nitrogen line. The reaction mixture was allowed to reflux for 24 hours. The color changed from light yellow to dark brown. No precipitate formed during the reaction. The resulting mixture was allowed to cool to room temperature and fractionally crystallized into two fractions giving the following analysis in Table 1.

Table 1. Fractional Crystallization of Product from the Reaction of Dimethylmagnesium with Benzonitrile in Diethyl Ether

Fractions	Sample Wt. (g)	Mg (%)	N.W.
1	1.5750	11.2	208
2	2.2850	11.6	214
Calcd. for $C_6H_5C(CH_3)NMgCH_3 \cdot Et_2O$		10.4	231

Ebullioscopic Determination of Molecular Association of $C_6H_5C(CH_3)NMgCH_3$ in Diethyl Ether

The apparent molecular weiths of the species present in this work were determined ebullioscopically in Et_2O at 740 mm[7] using a modified Cottrell boiling point elevation apparatus. Temperature changes were observed using a Beckman differential thermometer and the pressure was measured using a precision Wallace-Tiernan manometer. Solvent loss was prevented by recirculating ice-water in the condenser of the apparatus. Solvent and samples were introduced by weight through a septum on the apparatus from carefully weighed and sealed syringes. Details of the operation of this apparatus with organometallic systems have been presented elsewhere.[7]

The calculation was made using (Equation 1) which was derived in the usual manner by assuming an ideal, but not necessarily dilute, solution.

$$i = \frac{W_2 M_1}{W_1 M_2} \left(\frac{1}{e^{-\Delta T_B M_1 / 1000\ K_B} - 1} \right) \qquad (1)$$

The additional terms include M_2, the formula weight of the solute; M_1, the molecular weight of the solvent (74.12 g for diethyl ether); and K_B, the molal boiling point elevation constant (2.01 for diethyl ether at an internal nitrogen pressure of 740.0 mm). The association data are shown in Figure 1.

Extinction Coefficient of $C_6H_5C(CH_3)NMgCH_3$

A solution (25 ml, 0.111 M in diethyl ether) of $C_6H_5C(CH_3)NMgCH_3$ was prepared by the reaction of $(CH_3)_2Mg$ with C_6H_5CN in 2:1 ratio. The

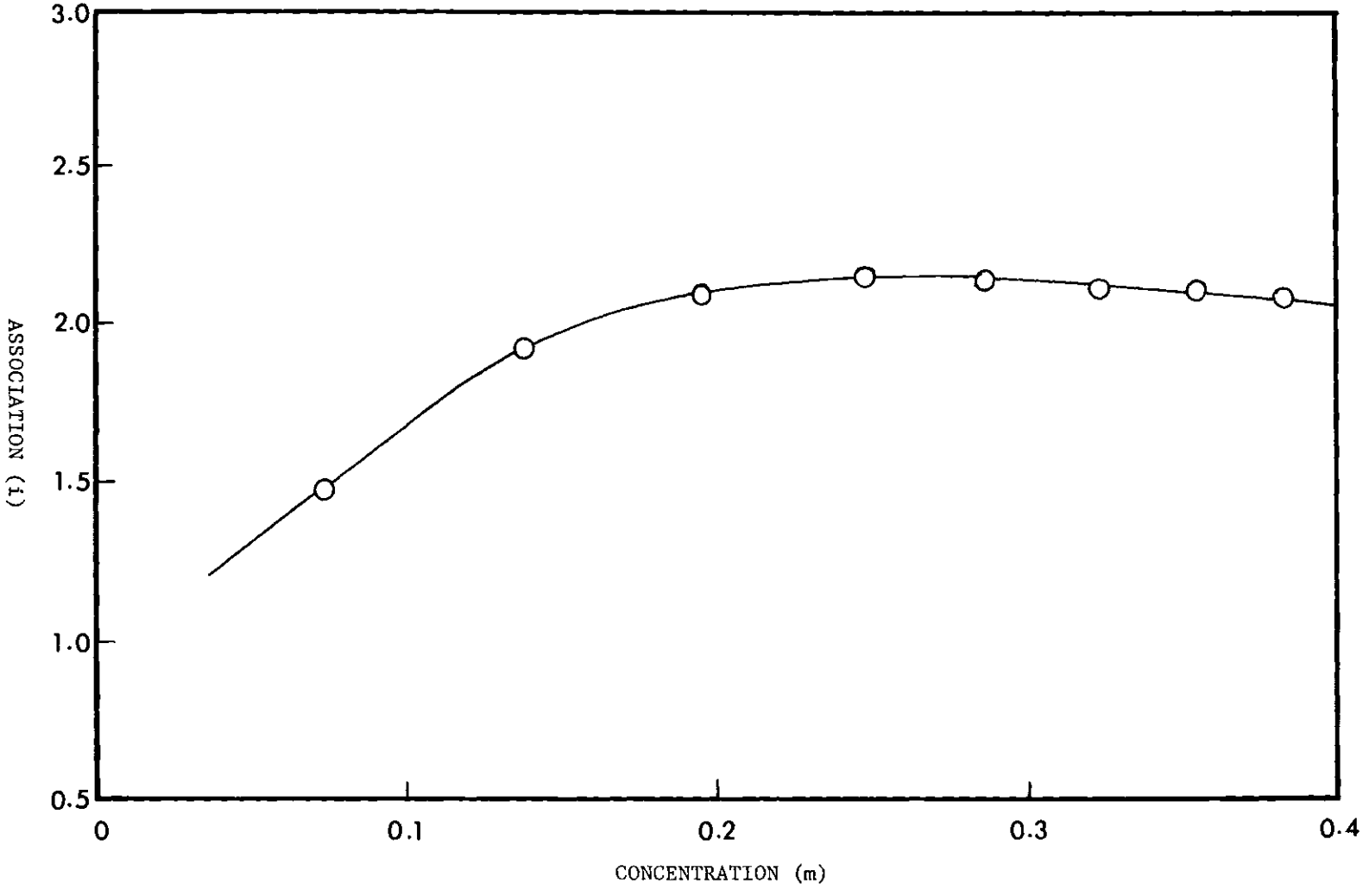


Figure 1. Association of $C_6H_5C(CH_3)NMgCH_3$ in Diethyl Ether

molar extinction coefficient of $C_6H_5C(CH_3)NMgCH_3$ was determined at several concentrations in diethyl ether at λ 338 mμ in the following fashion. A 4 ml portion of freshly distilled Et_2O was transferred to a UV cell which was sealed with a two-way teflon stopcock. A measured amount of $C_6H_5C(CH_3)NMgCH_3$ was then added to the UV cell via microliter syringe, and the absorbance of the solution measured at 338 mμ. Another measured amount of compound was added to the UV cell, and the absorbance measured again. The difference between the first absorbance and second absorbance is attributed to the second amount added. The subtraction method is better than a single measurement since it can avoid errors due to hydrolysis of the sample. The average value of the molar extinction coefficient of $C_6H_5C(CH_3)NMgCH_3$, calculated using Beer's Law, is 127 ± 0.4.

CHAPTER III

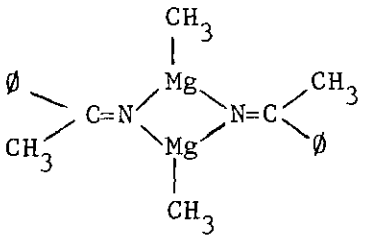
RESULTS AND DISCUSSION

Physical Properties of the Reaction Products

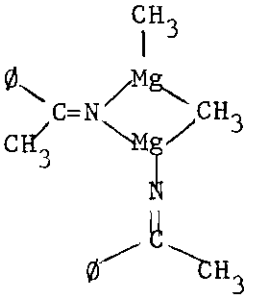
The reaction product of $(CH_3)_2Mg$ with benzonitrile has been investigated by fractional crystallization, molecular association and nmr.

The results of the molecular association study are shown in Figure 1, where the association constant (i) (observed molecular weight/calculated molecular weight) is plotted vs. solute concentration (molality). The data show that the compound $C_6H_5C(CH_3)NMgCH_3$ is predominantly monomeric at low concentration, and exists exclusively as dimeric species when the concentration increases over 0.15 m.

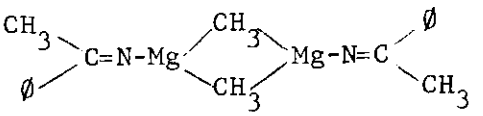
The association of organomagnesium compounds in diethyl ether has been reported recently for alkylmagnesium alkoxides, thio- and aminomagnesium alkyls. The association is explained on the basis of available electrons on oxygen,[8,9] sulphur[10] and nitrogen[11] interacting with the vacant orbitals of Mg. Some previous workers have also point out that nitrogen as a bridging group is better than halogen and alkyl groups. The structure of the dimer of $C_6H_5C(CH_3)NMgCH_3$, which exists in ether solution, can be represented by (A), (B), or (C).



(A)



(B)

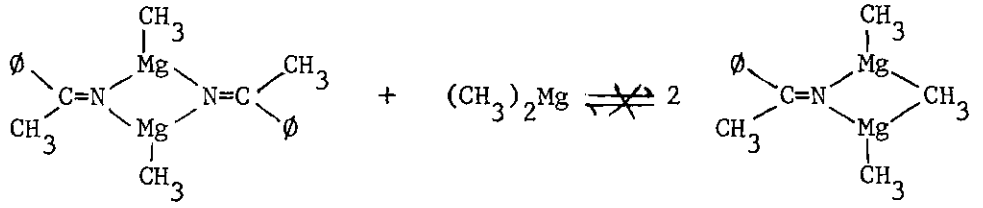


(C)

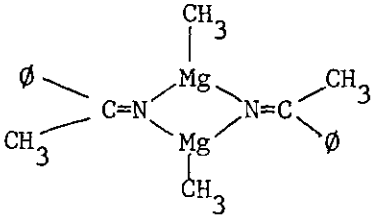
Although structure (A) would be expected to be the most stable, there exists no direct evidence to substantiate such a choice.

Recently Wade and coworkers have also reported that azomethine derivatives of organometallic compounds (M = Li, Be, Al and B) associate in diethyl ether through a nitrogen bridge.[12-16] For example, benzonitrile reacts with Me_3Al, Et_3Al, Ph_3Al, and Me_2AlCl to form 1:1 adducts which rearrange at 130-200° to form benzylidene amino derivatives $(PhMeC{:}N{\cdot}AlMe_2)_2$, $(PhCH{:}N{\cdot}AlEt_2)_2$, $(Ph_2C{:}CN{\cdot}AlPh_2)_2$ and $(PhMeC{:}N{\cdot}AlMeCl)_2$ respectively. The nmr spectra of the benzylideneamino-derivatives support a nitrogen-bridged structure for the dimers.[17] The success of structure determination by nmr spectroscopy for a nitrogen-bridged dimer in the reaction of organoaluminum with nitrile encouraged a similar study with the organomagnesium compound. Low temperature 100-MHz nuclear magnetic resonance spectroscopy was employed in the study of the $C_6H_5C(CH_3)NMgCH_3$ structure. The sample concentration employed was 0.4 M. At -100° the nmr spectrum of pure $C_6H_5C(CH_3)NMgCH_3$ shows three peaks at 11.33τ, 11.46τ and 11.72τ attributed to this Mg-CH_3 group. The intensity at 11.46τ is eight fold larger than those at 11.33τ and 11.72τ; the two smaller peaks have approximately equal intensity. Nmr spectra of mixtures of $C_6H_5C(CH_3)NMgCH_3$ and $(CH_3)_2Mg$ have also been obtained in the stoichiometry ratio of $C_6H_5C(CH_3)NMgCH_3$ to $(CH_3)_2Mg$ of 1:1, 1:2 and 1:3. In these spectra the chemical shifts of the peaks only slightly changed. The relative ratios of the peaks are nearly constant; only the peak attributed to $(CH_3)_2Mg$ increases as ratio of $(CH_3)_2Mg$ to $C_6H_5C(CH_3)NMgCH_3$ increases. The spectra reveal that addition of $(CH_3)_2Mg$ does not change the structure of the dimeric species of $C_6H_5C(CH_3)NMgCH_3$ in diethyl ether. Thus it

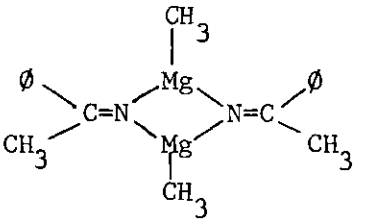
seems reasonable to assume the following equilibrium does not exist for the alkyl-nitrogen mixed bridge system.



From fractional crystallization, the compound $C_6H_5C(CH_3)NMgCH_3$ in the solid state was found to be associated with one ether molecule. From all of the available information it appears that $C_6H_5C(CH_3)NMgCH_3$ is dimeric in diethyl ether and can be represented by structures such as AI and AII.



AI



AII

The nmr peak at 11.46τ which has a relatively large intensity is due to the two equivalent Mg-methyl groups in a trans-structure (AI) and the two smaller peaks at 11.33τ and 11.72τ which have approximately equal intensity are due to the two non-equivalent sets of CH_3-Mg groups in a cis-structure (AII). The nmr also reveals that trans structure is more stable due to the relatively large intensity.

Complex between Benzonitrile and Dimethylmagnesium

In seeking evidence for a complex between benzonitrile and

dimethylmagnesium, the spectra of benzonitrile (8.31×10^{-4} M) and dimethylmagnesium, (8.23×10^{-4} M) in diethyl ether were obtained over the range 220-350 mμ. The spectrum of the mixture was also scanned immediately after the two reactants were mixed together. The absorption of the mixture in the region 240-285 mμ was distinctly larger than the sum of the components. The change in abosrbance of the mixture of benzonitrile and dimethylmagnesium was apparently larger than the change of absorption for benzonitrile-methylmagnesium bromide and benzonitrile-$MgBr_2$ mixtures under the same condition. The UV data indicate that complexation does occur between $(CH_3)_2Mg$ and benzonitrile, but quantitative evaluation of the extent of complexation was not possible.

Kinetics

The kinetic studies in excess $(CH_3)_2Mg$, using gas chromatographic analysis of products, show that benzonitrile and dimethylmagnesium react to form the expected alkylation product $C_6H_5C(CH_3)NMgCH_3$ in quantitative yield without the side reactions of enolization or reduction. The product yield studies show that the same is true when C_6H_5CN and $(CH_3)_2Mg$ react in 1:1 and 2:1 mole ratios. These studies demonstrate that both groups on $(CH_3)_2Mg$ are reactive, although the second group reacts much more slowly with C_6H_5CN. The ketimine group on magnesium should decrease the electrophilic character of the Mg atom and thereby reduce its tendency to react with nitriles. It also appears unlikely that equilibrium (2) leads to a detectable concentration of $(CH_3)_2Mg$.

$$2\ \phi\text{-}\underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}\text{=N-Mg-}CH_3 \rightleftharpoons (\phi\text{-}\underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}\text{=N})_2Mg + (CH_3)_2Mg \qquad (2)$$

When reaction occurs in excess benzonitrile, significant changes occur in the visible and ultraviolet spectra during the course of the reaction. Separate solutions of $(CH_3)_2Mg$ in ether and concentrated solutions of C_6H_5CN show no absorbance at wavelengths longer than 290 mμ. After mixing solutions of $(CH_3)_2Mg$ and C_6H_5CN, a broad band slowly appears in the region of 300 mμ to 450 mμ and increases with time. The absorbances of reaction mixtures were measured at four different wavelengths (325 mμ, 338 mμ, 414 mμ and 430 mμ) over a period of 30 days. At 325 mμ and 338 mμ the absorbances increased with time, each finally reaching an almost constant value after sufficient time. At 414 mμ and 430 mμ the absorbances increased with time, reached a maximum point, and then decreased steadily (Figure 2). The shapes of these curves suggest a greater complexity to the reaction than expected; at least three reactions must be occurring over the time period shown.

Before meaningful kinetic data could be obtained by UV measurements it was necessary to determine how these reactions were related to the addition reaction of interest. For this purpose measurements of both product yield and absorbancy were made on a sample undergoing reaction during the period of time that the absorbancy was rising to its maximum. Small portions of the sample in the UV cell were withdrawn at appropriate intervals of time, quenched and hydrolyzed in saturated NH_4Cl solution, and analyzed for acetophenone by gas chromatography. The yield of product is shown in Table 2, along with the measured absorbancies.

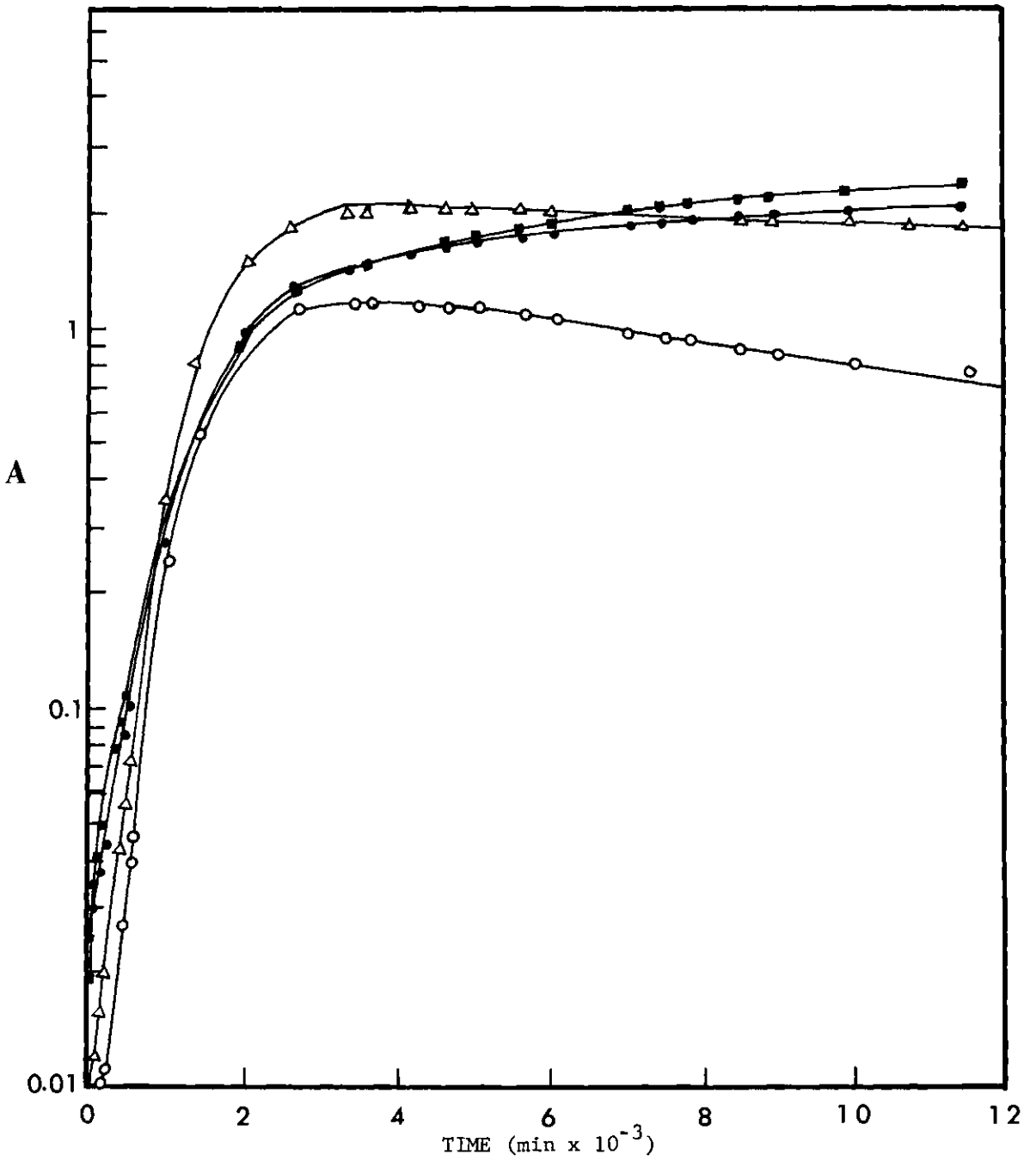


Figure 2. The Absorbance of the Reaction Mixtures of Dimethylmagnesium with Excess Benzonitrile at Different Wavelengths; ●, at 325 mμ; ■, at 338 mμ; △, at 414 mμ; O, at 430 mμ

Table 2. The Correlation between Absorbance and Percentage of Product in the Reaction of Benzonitrile (0.0900 M) With Dimethylmagnesium (2.47×10^{-3} M)

Reaction Time (Min.)	Absorbance 338 mμ	Absorbance 430 mμ	Product (%) Found	Product (%) Calculated*
687	0.346	0.136	37	49
1011	0.680	0.465	43	50
1284	1.034	1.027	38	47
1487	1.632	1.621	36	43
1698	2.20	2.30	<10	39

*Product (%) was computed according to Equation 4.

The fact that the absorbancies increase but the percentage of the product does not reveals that the strong absorbance in the latter stage of the reaction is not due to the main product. It is attributed to some condensed products[18] which have high molar extinction coefficients.

Since the initial reaction is the one of greatest interest, the rate during the first 30% of the reaction was measured. Two methods were used. The first was a spectrophotometric method, utilizing measurements at 338 mμ. The molar extinction coefficient, ε, of the initial product, $C_6H_5C(CH_3)NMgCH_3$, had been determined independently. If reaction proceeded solely to this product the final absorbancy, Af, would be $Af = \varepsilon C$, where C is the initial concentration of dimethylmagnesium. Plots of log (Af - A) versus t were linear, as expected, during the early stages of the reaction, and from the slopes of these lines the

pseudo-first-order rate constant, k_N, could be determined.

The second method was performed simultaneously with the first. Individual samples of the reaction mixture were withdrawn at appropriate intervals of time, quenched in saturated ammonium chloride, and the amount of acetophenone measured by gas chromatography. Pseudo-first-order rate constants were calculated from the first-order equation.

The results obtained by these methods are summarized in Table 3. The pseudo-first-order behavior in the two methods demonstrates that the reaction is first-order in $(CH_3)_2Mg$. The constancy of $k_N/[N]_o$ demonstrates that the reaction is first-order in nitrile. The agreement in the values obtained by the two methods is satisfactory.

Table 3. Rate Constants for Reaction of $(CH_3)_2Mg$ with Excess of Benzonitrile at 25°

Run	$[(CH_3)_2Mg]_o$	$[C_6H_5CN]_o$	$\frac{k_N}{[N]_o} \times 10^2$ 1. mole^{-1} min^{-1} by G.C.	$\frac{k_N}{[N]_o} \times 10^2$ 1. mole^{-1} min^{-1} by U.V. at 338mμ
1	0.00158	0.0334	1.95	1.81
2	0.00267	0.0660	1.87	1.79
3	0.00267	0.100	1.76	1.74
4	0.00267	0.125	1.74	1.76
5	0.00267	0.168	1.99	1.82
6	0.00267	0.188	1.86	1.78
7	0.00267	0.213	2.08	1.72
		Ave.	1.89 ± 0.10	1.77 ± 0.03

Although the later stage of the reaction was not the major interest in this work, the UV absorbancy data was analyzed for any additional information it might provide. The data taken at 430 mμ was the most valuable for this purpose. The absorbancy first increased with time, then reached a maximum value and then decreased steadily. In the very late stage of the reaction, plots of log Abs vs. time were linear for each run. An observed first-order rate constant, k_3, could then be extracted from this portion of each reaction. The line defining k_3 was extrapolated to zero reaction time and from its value at appropriate times was substracted the measured absorbancy. Plots of log (extrapolated line - Abs) vs. time resolved into another first-order straight line with curvature at initial stage. The line defining k_2 was extrapolated to zero reaction time and from its value was substracted the values on the curve k_2. Plots of log [extrapolated line k_2 - (extrapolated line k_3 - Abs)] vs. time resolved into a third first-order component, k_1. The resolution of k_1, k_2 and k_3 for a specific experiment is demonstrated in Figure 3. The results obtained from this mode of analysis summarized in Table 4.

If this analysis is correct it suggests a series of pseudo-first-order reactions involving three products. Support for this view is

$$(CH_3)_2Mg \xrightarrow[k_1]{C_6H_5CN} P_1 \xrightarrow[k_2]{C_6H_5CN} P_2 \xrightarrow[k_3]{C_6H_5CN} P_3 \qquad (3)$$

provided by the consistency of the results in Table 4 as the C_6H_5CN concentration is varied from 0.0346 to 0.460 M, and by the good agreement of the value for $k_1/[N]_o$ obtained with the values shown in Table 3.

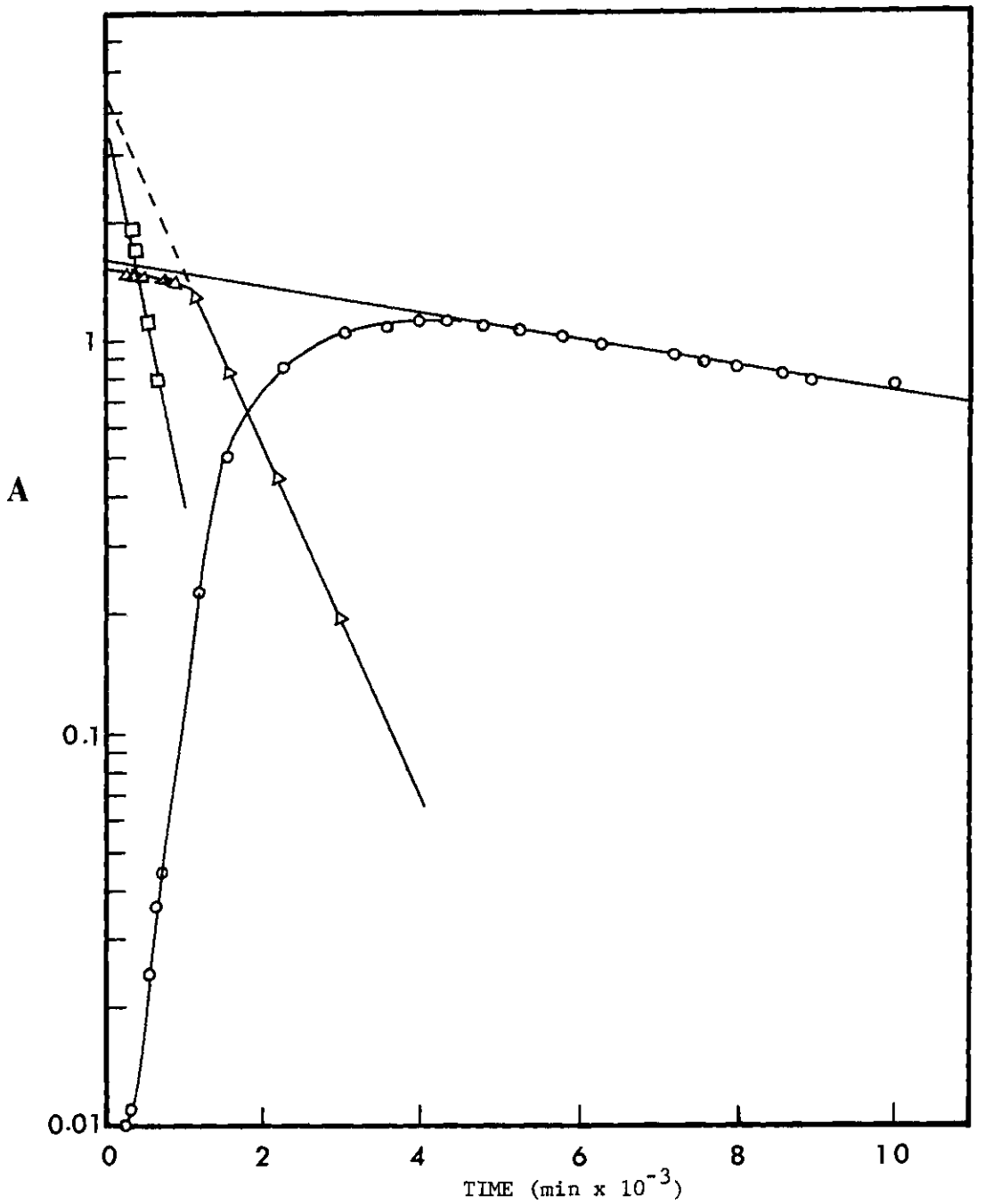


Figure 3. Demonstration of Reaction Rates in the Reaction of Dimethylmagnesium with Excess Benzonitrile at 430 mμ

Table 4. Observed Rate Constants for the Various Organometallic Species Involved in the Reaction of 8.22×10^{-4} M $(CH_3)_2Mg$ with Varying Excess of Nitrile at 430 mμ

Run	$[C_6H_5CN]_o$	$\frac{k_1}{[N]_o} \times 10^2$ $l.mole^{-1}min^{-1}$	$\frac{k_2}{[N]_o} \times 10^3$ $l.mole^{-1}min^{-1}$	$\frac{k_3}{[N]_o} \times 10^4$ $l.mole^{-1}\ min^{-1}$
8	0.0346	1.79	8.96	6.91
9	0.0461	1.64	9.10	7.07
10	0.0900	1.76	8.80	6.60
11	0.113	1.92	8.07	5.67
12	0.140	1.66	7.87	6.25
13	0.205	1.83	8.35	
14	0.298	1.83	9.06	
15	0.460	1.79	8.15	6.33
	Ave.	1.78	8.55	6.47

Each step of the reaction is first-order in the appropriate organometallic species; i.e., $(CH_3)_2Mg$, P_1, or P_2, and first-order in C_6H_5CN. The product P_1 was shown to be $C_6H_5C(CH_3)NMgCH_3$ by gas chromatography. The product P_2 must be a condensation product that does not give acetophenone on hydrolysis, in order to account for the product yield shown in Table 2. Using this assumption, and the rate constants k_1 and k_2 from Table 4, the expected yield of acetophenone can be calculated from the equation

$$\frac{[P_1]}{[D]_o} = \frac{k_1}{k_1 - k_2} \left(e^{-k_2 t} - e^{-k_1 t} \right) \qquad (4)$$

These are shown in the last column of Table 2. The structures of P_2 and P_3 are unknown.

A detailed study of the reaction of C_6H_5CN with excess $(CH_3)_2Mg$ was undertaken. The kinetic data were obtained by quenching individual samples of the reaction mixture in saturated NH_4Cl solution at appropriate intervals of time and measuring the amount of nitrile in each sample by gas chromatographic analysis. Samples were taken over the range 5-80% reaction. In each kinetic experiment the amount of nitrile was found to decrease in a first-order fashion. The pseudo-first-order rate constant,[19] k_D, was computed by the following equation:

$$k_D = \frac{1}{t} \ln \frac{[C]_o}{[C]} = \frac{1}{t} \ln \frac{[C]_o \, 100}{[C]_o \, x} = \frac{1}{t} \ln \frac{100}{x} \qquad (5)$$

where $[C]_o$ and $[C]$ are the initial concentration and the concentration at time t respectively. The x is the % of unreacted nitrile.

In the first set of experiments the rate constant was measured at a constant concentration of $(CH_3)_2Mg$ while the initial C_6H_5CN concentration was varied over better than a four fold range. Surprisingly, the rate constant was found to depend on the initial concentration of C_6H_5CN (Table 5). The dependence of rate constant on the initial C_6H_5CN concentration can be rationalized by assuming that the reaction rate with C_6H_5CN concentration below 10^{-3} M is affected by the impurities in the magnesium. Transition metal impurities in Mg are Fe, Co and Ni, each of which is less than 2 p.p.m. In 0.0445 M $(CH_3)_2Mg$ the concentration of each impurity would than be about 10^{-7}. In the remaining kinetic studies the concentration of C_6H_5CN employed was higher than 10^{-3} M, since under these conditions the rate constant seems to be independent of the concentration of C_6H_5CN.

Table 5. Rate Constants for the Reaction of $(CH_3)_2Mg$ at Constant Concentration (0.0445 M) with a Variable Concentration of Benzonitrile.

Run	$[C_6H_5CN]_o \times 10^4$, M	$k_D \times 10^4$, min^{-1}
16	5.125	10.59
17	10.25	6.094
18	15.37	4.561
19	19.84	4.575
20	22.03	4.444

In Table 6 the results of experiments are summarized in which the concentration of $(CH_3)_2Mg$ (in excess) is varied. Comparison of the values of $k_D/[(CH_3)_2Mg]_o$ with the bimolecular rate constant, 1.77×10^{-2} $l.mole^{-1}min^{-1}$, obtained from the studies in excess benzonitrile, indicates that $(CH_3)_2Mg$ is not solely present as monomer. This conclusion agrees with association studies of dimethylmagnesium in diethyl ether solution reported by other workers.[1] At 0.1 M the association constant, i, for $(CH_3)_2Mg$ in ether solution is 1.43. This means that at this concentration the $(CH_3)_2Mg$ solution contains monomer and some associated species. Due to the small value of i, it seems reasonable to assume that an equilibrium between monomer and dimer exists at or below 0.1 M, with the higher associated species in negligible amount. If we assume that reaction occurs only through the monomeric species, and that the bimolecular rate constant is 1.77×10^{-2} $l.mole^{-1}min^{-1}$, then the concentration of monomer, $[M]_o$, can be calculated from the value of k_D. Values of $[D]_o$ and i can be calculated from this model. The results of these calculations are shown in Table 6. The i values are in good agreement with values obtained by the association study; i = 1.11 at 0.0168 M $(CH_3)_2Mg$, and i = 1.39 at 0.0609 M. Although these results do not rule out the possibility that some reaction occurs via the dimer, the results are such that the amount of reaction proceeding by this path must be very small.

From these kinetic results with $(CH_3)_2Mg$ and the results from the methyl bromide Grignard performed at comparable concentration conditions, an approximate calculation of the position of the Schlenk equilibrium for methylmagnesium bromide is possible. The % of $(CH_3)_2Mg$ in

Table 6. Rate Constants for the Reaction of Benzonitrile with Excess Dimethylmagnesium

Run	$[(CH_3)_2Mg]_o$	$[C_6H_5CN]_o \times 10^3$	$k_D \times 10^4$ min^{-1}	$\frac{k_D \times 10^2}{[(CH_3)_2Mg]_o}$ $1.M^{-1}min^{-1}$	$[M]_o \times 10^2$	i
21	0.101	1.34	9.26	0.915	5.23	1.33
22	0.0882	1.39	7.94	0.900	4.49	1.32
23	0.0737	1.40	7.02	0.952	3.96	1.30
24*	0.0562	1.46	6.04	1.08	3.42	1.24
a	0.0444		4.28	0.964	2.42	1.29
26	0.0351	1.51	3.66	1.05	2.07	1.25

*Contained $\phi C(CH_3)NMgCH_3$ of which concentration was 1.50×10^{-3} M.

a The average of Runs 18 and 25

Grignard solution is $2.41 \times 10^{-3} \times 0.60/1.77 \times 10^{-2} = 8.2\%$ which is in very good agreement with Holm's value,[20] but somewhat different from Smith and Becker's value.[21] Even though this percentage is not established with great accuracy from the kinetic results, the fact that the Schlenk equilibrium is predominantly favorable to the RMgX side is quite definite.

CHAPTER IV

CONCLUSION

The reaction of dimethylmagnesium with benzonitrile in diethyl ether at 25° was examined in detail. Kinetic studies have been carried out under pseudo-first-order conditions using either excess dimethylmagnesium or excess nitrile and the reaction was found to be first order in nitrile and first order in dimethylmagnesium. The ultraviolet spectra of reacting mixtures showed that complexation between reactants does occur. The physical properties of the reaction product have also been studied. The association study showed that the product is predominantly monomeric at low concentration and exclusively dimeric at high concentration. Association was shown by variable temperature nmr to exist via nitrogen bridge bonds.

APPENDIX

Table 7. Reaction of Dimethylmagnesium with Excess Benzonitrile at 25° (Run 1 and 2)

U. V. Analysis		G. C. Analysis	
Time (min)	Absorbance at 338 mμ	Time (min)	Reaction (%)
73	0.015	63	3.22
86	0.017	83	5.18
114	0.020	106	8.75
150	0.024	147	10.80
175	0.028	243	16.10
243	0.036	361	21.54
358	0.049		
Af = 0.200	$[N]_o$ = 0.0334 M	$[(CH_3)_2Mg]_o = 1.58 \times 10^{-3}$ M	
18	0.032	19	1.80
41	0.044	37	4.62
56	0.051	57	6.73
70	0.056	77	9.01
84	0.061	95	12.13
101	0.066	122	13.87
122	0.072	155	18.00
140	0.076	181	18.88
220	0.094	251	23.10
259	0.100		
Af = 0.338	$[N]_o$ = 0.066 M	$[(CH_3)_2Mg]_o = 2.67 \times 10^{-3}$ M	

Table 8. Reaction of Dimethylmagnesium with Excess Benzonitrile at 25° (Run 3)

U. V. Analysis		G. C. Analysis	
Time (min)	Absorbance at 338 mμ	Time (min)	Reaction (%)
5	0.016	16	6.50
22	0.033	30	8.40
36	0.043	49	10.05
46	0.050	63	13.45
58	0.056	90	17.48
75	0.066	123	21.72
89	0.071	158	26.00
99	0.076		
109	0.080		
119	0.084		
129	0.088		
137	0.091		

Af = 0.338 $[N]_o$ = 0.100 M $[(CH_3)_2Mg]_o$ = 2.67 x 10^{-3} M

Table 9. Reaction of Dimethylmagnesium with Excess Benzonitrile at 25° (Run 4 and 5)

U. V. Analysis		G. C. Analysis	
Time (min)	Absorbance at 338 mμ	Time (min)	Reaction (%)
8	0.048		
18	0.055	24	5.10
26	0.064	35	7.23
36	0.066	47	9.91
45	0.069	59	11.95
61	0.077	71	13.60
72	0.085	115	22.00
116	0.103	130	25.30
132	0.110	148	28.00
147	0.117		
Af = 0.338	$[N]_o$ = 0.125 M	$[(CH_3)_2Mg]_o$ = 2.67 x 10^{-3} M	
9	0.043	13	5.57
17	0.054	23	6.78
29	0.066	34	11.06
37	0.072	43	14.20
46	0.080	55	16.81
57	0.087	67	19.27
69	0.095	84	28.91
82	0.104	125	35.89
126	0.129		
135	0.134		
Af = 0.338	$[N]_o$ = 0.168 M	$[(CH_3)_2Mg]_o$ = 2.67 x 10^{-3} M	

Table 10. Reaction of Dimethylmagnesium with Excess Benzonitrile at 25° (Run 6 and 7)

U. V. Analysis		G. C. Analysis	
Time (min)	Absorbance at 338 mμ	Time (min)	Reaction (%)
7	0.046	19	6.50
16	0.059	29	9.73
24	0.067	40	12.69
32	0.075	50	16.47
44	0.085	64	17.21
53	0.091	76	23.83
63	0.098	105	27.36
71	0.103		
92	0.115		
104	0.122		
Af = 0.338	$[N]_o$ = 0.188 M	$[(CH_3)_2Mg]_o$ = 2.67 x 10^{-3} M	
13	0.055	14	6.73
20	0.065	24	13.48
29	0.076	34	14.94
40	0.088	44	17.59
47	0.094	66	25.97
58	0.103	81	30.60
68	0.112		
79	0.120		
91	0.131		
108	0.141		
Af = 0.338	$[N]_o$ = 0.213 M	$[(CH_3)_2Mg]_o$ = 2.67 x 10^{-3} M	

Table 11. Reaction of Benzonitrile with Excess Dimethylmagnesium at 25° (Run 16 and 17)

Time, minutes	Reaction (%)	$k_D \times 10^4$, min^{-1}
159	5.69	10.30
295	18.79	10.62
459	29.63	9.95
729	51.76	11.44
848	53.59	10.29
1373	75.19	10.92
1634	80.28	10.58
		Ave. 10.59 ± 0.346
$[N]_o = 5.125 \times 10^{-4}$ M		$[(CH_3)_2Mg]_o = 4.45 \times 10^{-2}$ M
156	9.98	6.740
295	20.21	
456	24.29	6.102
728	34.73	5.860
844	38.85	5.827
1373	55.91	5.965
1631	62.83	6.068
		Ave. 6.094 ± 0.218
$[N]_o = 1.025 \times 10^{-3}$ M		$[(CH_3)_2Mg]_o = 4.45 \times 10^{-2}$ M

Table 12. Reaction of Benzonitrile with Excess Dimethylmagnesium at 25° (Run 18 and 19)

Time, minutes	Reaction (%)	$k_D \times 10^4$, min^{-1}
222	13.83	4.725
472	23.59	4.769
856	33.49	4.251
1689	54.97	4.464
3031	74.04	4.304
3483	80.52	4.570
3758	84.48	4.841
		4.561 ± 0.189
$[N]_o = 1.537 \times 10^{-3}$ M		$[(CH_3)_2Mg]_o = 4.45 \times 10^{-2}$ M
260	21.66	
431	24.46	4.624
698	29.64	
899	40.50	4.872
1617	55.58	4.516
1834	59.81	4.527
2271	67.36	4.573
3047	76.91	4.544
3392	79.04	4.367
		Ave. 4.575 ± 0.099
$[N]_o = 1.984 \times 10^{-3}$ M		$[(CH_3)_2Mg]_o = 4.45 \times 10^{-2}$ M

Table 13. Reaction of Benzonitrile with Excess Dimethylmagnesium at 25° (Run 20)

Time, minutes	Reaction (%)	$k_D \times 10^4$, min^{-1}
409	17.20	4.615
545	20.95	4.314
666	26.10	4.541
879	31.00	4.221
1413	46.60	4.440
1712	53.40	4.460
1952	58.00	4.444
2243	62.60	4.385
3263	77.50	4.571
		Ave. 4.444 ± 0.0919

$[N]_o = 22.03 \times 10^{-4}$ M $\quad [(CH_3)_2Mg]_o = 4.45 \times 10^{-2}$ M

Table 14. Reaction of Benzonitrile with Excess Dimethylmagnesium at 25° (Run 21 and 22)

Time, minutes	Reaction (%)	$k_D \times 10^4$, min^{-1}
53	7.20	
130	11.30	9.224
189	14.91	8.543
258	22.60	9.926
444	35.80	9.981
539	37.13	8.610
639	45.18	9.407
1226	66.81	8.996
1441	74.15	9.388
		9.259 ± 0.416
$[N]_o = 1.34 \times 10^{-3}$ M	$[(CH_3)_2Mg]_o = 0.101$ M	
153	11.20	7.764
247	18.68	8.372
329	26.86	
1208	60.43	7.675
1432	67.96	7.948
1677	72.23	7.640
2016	81.05	8.251
		Ave. 7.942 ± 0.249
$[N]_o = 1.39 \times 10^{-3}$ M	$[(CH_3)_2Mg]_o = 8.82 \times 10^{-2}$ M	

Table 15. Reaction of Benzonitrile with Excess Dimethylmagnesium at 25° (Run 23)

Time (min)	Reaction (%)	$k_D \times 10^4$, min^{-1}
53	6.93	6.241
121	14.74	
255	20.30	7.379
338	25.22	7.452
466	30.01	6.826
626	41.32	7.897
926	50.16	7.102
1376	63.39	7.021
1668	66.23	6.276
2168	79.24	7.072
3168	89.14	6.883
		Ave. 7.015 ± 0.367

$[N]_o = 1.40 \times 10^{-3}$ M $\quad [(CH_3)_2Mg]_o = 7.37 \times 10^{-2}$ M

Table 16. Reaction of Benzonitrile with Excess Dimethylmagnesium at 25° (Run 24)

Time, minutes	Reaction (%)	$k_D \times 10^4$, min^{-1}
83	3.69	
238	16.58	
324	16.79	5.673
454	24.93	6.316
901	40.39	5.742
1124	49.53	6.084
1414	59.41	6.377
1775	65.59	6.010
2390	75.42	5.871
3167	86.32	6.281
		Ave. 6.044 ± 0.220

$[N]_o = 1.46 \times 10^{-3}$ M

$[(CH_3)_2Mg]_o = 5.62 \times 10^{-2}$ M

$[\emptyset C(CH_3)NMgCH_3]_o = 1.50 \times 10^{-3}$ M

Table 17. Reaction of Benzonitrile with Excess Dimethylmagnesium at 25° (Run 25 and 26)

Time, minutes	Reaction (%)	$k_D \times 10^4$, min^{-1}
140	4.00	
656	22.23	3.833
1376	44.35	4.253
1609	47.92	4.055
1888	52.84	3.981
2152	57.84	4.013
2850	66.95	3.885
3085	69.10	3.807
4679	84.80	4.026
		3.982 ± 0.105
$[N]_o = 1.54 \times 10^{-3}$ M		$[(CH_3)_2Mg]_o = 4.42 \times 10^{-2}$ M
72	4.70	
269	11.20	
379	14.00	3.979
484	16.50	3.726
815	25.00	3.530
1388	39.92	3.671
1669	44.50	3.539
1954	51.00	3.651
3150	67.20	3.539
		3.662 ± 0.111
$[N]_o = 1.51 \times 10^{-3}$ M		$[(CH_3)_2Mg]_o = 3.51 \times 10^{-2}$ M

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